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EXPLOSIVES

THEIR MANUFACTURE, PROPERTIES TESTS AND HISTORY

BY

ARTHUR MARSHALL

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Chemical Inspector, Indian Ordnance Department

WITH 137 ILLUSTRATIONS

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PREFACE

SINCE the late Mr. Oscar Guttmann published his work on the *Manufacture of Explosives* in 1895 no comprehensive book on this subject has appeared in English. In the interval the explosives industry has undergone many changes: every branch of it has developed enormously—even that of black powder; and scientific investigations have thrown light on many of the problems that arise in the manufacture and use of explosives. Especially during the last few years many obscure points have been cleared up. It is hoped therefore that the present work will be found to supply a real want.

In a single book of moderate size it is not possible to treat in detail every point that arises in connexion with explosives. Consequently it has been necessary to restrict its scope in some directions. The methods of using explosives belong rather to the subjects of ballistics, blasting, etc., and their full discussion would alone require a larger work than this. Therefore they have only been referred to briefly. Details of manufacture, although often of much practical importance, can only be learnt properly in the factory: consequently they have been omitted in many cases. Proposals made in patent specifications have not been dealt with unless they possess practical or theoretical importance; for more detailed information concerning patents relating to explosives the reader should refer to works such as those of R. Escales. Subjects which are treated fully in the ordinary scientific or technical text-books have only been dealt with in so far as they throw new light on problems connected with explosives.

On the other hand, an endeavour has been made to increase the usefulness of the book by collecting allied facts from scattered sources, and placing them in juxtaposition with one another. Some subjects, which are only mentioned briefly, or not at all, in other books have been treated more fully than their intrinsic importance would otherwise have called for. Numerous references

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to original papers, etc., have been given to assist those who require more detailed information concerning the subjects dealt with. Considerable space has been given to matters connected with the difficult and intricate question of the stability of nitro-cellulose and allied compounds.

I am indebted to my wife for her valued help in revising the book. My thanks are also due to Mr. W. Rintoul, Mr. J. Thorburn, and Mr. W. R. Moore for assistance in revising the proofs.

It is my earnest hope that the book may be of help to my country in the present time of emergency.

A. MARSHALL.

NAINI TAL, INDIA.

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LIST OF PRINCIPAL ABBREVIATIONS

JOURNALS, ETC.

A. and E.	*Arms and Explosives.*
Ang.	*Zeitschrift für angewandte Chemie.*
A.R.	*Annual Reports of H.M. Inspectors of Explosives.*
B.	*Berichte of the German Chemical Society.*
Bull.	*Bulletin of U.S. Bureau of Mines.*
Chem. Ind.	*Die chemische Industrie.*
C.R.	*Comptes Rendus.*
C.Z.	*Chemiker-Zeitung.*
J.C.S.	*Journal of the Chemical Society.*
J.S.C.I.	*Journal of the Society of Chemical Industry.*
P. et S.	*Mémorial des Poudres et Salpêtres.*
Phil. Trans.	*Philosophical Transactions of the Royal Society.*
Proc. R.S.	*Proceedings of the Royal Society.*
S.R.	*Special Reports of H.M. Inspectors of Explosives.*
S.S.	*Zeitschrift für das gesamte Schies- und Sprengstoffwesen.*
Trans. R.S.	*Transactions of the Royal Society.*

BOOKS

Chalon.	*Les Explosifs Modernes.*
Cundill and Thomson	*Dictionary of Explosives.*
Hime.	*Gunpowder and Ammunition*, by Lieut.-Colonel Hime.
Manufacture.	*The Manufacture of Explosives*, by O. Guttmann.
Monumenta.	*Monumenta Pulveris Pyrii*, by O. Guttmann.
Twenty Years Progress.	*Twenty Years Progress in Explosives*, by O. Guttmann.
Rise and Progress.	*The Rise and Progress of the British Explosives Industry.*
Worden.	*The Nitro-cellulose Industry*, by Worden.
Zschokke.	*Militarische Spengtecknik*, by B. Zschokke.

OTHER ABBREVIATIONS

b.p.	boiling-point.	G/c.	guncotton.
c.c.	cubic centimetres.	m.p.	Melting-point.
coll. cot.	collodion cotton.	N/c.	Nitrocellulose.
D/n/g.	dinitroglycerine.	N/g.	Nitroglycerine.
D/n/t.	dinitrotoluene.	sp. gr.	Specific gravity.
g.	grammes.	T/n/t.	Trinitrotoluene.

Temperatures are always in degrees Centigrade unless otherwise stated.

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PART I

HISTORICAL

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CHAPTER I

EARLY HISTORY

Gunpowder : Confusion of terms : Incendiary mixtures : Greek fire : Saltpetre : The Chinese : The Indians : Roger Bacon : The Arabs : Chinese fire-works : Invention of fire-arms : Early powder-mills : Summary : Gibbon

Gunpowder.

UNTIL the nineteenth century the only explosive practically known was ordinary gunpowder, a mixture of saltpetre, sulphur and charcoal. Two of these constituents have been known from time immemorial, for sulphur occurs native in a state of considerable purity in some volcanic districts, and charcoal is made by simply heating wood. The early history of gunpowder and explosives generally is therefore closely connected with the discovery of methods of preparing and purifying saltpetre.

Confusion of terms.

The investigation of this and other similar matters is rendered difficult not only by the scarcity of early records, but also by the great uncertainty as to their true interpretation. When saltpetre, gunpowder and guns were discovered or invented, new words were not made, but old terms were adopted which had previously been used for somewhat similar objects. Our word "powder," for instance, means any dust-like material, but the term smokeless powder is now used to denote a class of substances which have nothing in common with dust. "Gun" is from the old English "gonne," which was used to denote an instrument for throwing projectiles before the introduction of gunpowder. Similarly the Arabic "bunduq" (بندوق) now used for any rifle or sporting gun, formerly meant a pellet shot from a small catapult used for sporting purposes. Saltpetre (sal petræ) merely means salt of the rock, and the other Latin term for the same material, "nitrum" (nitron, nitre), formerly meant soda or any other white efflorescence. Both nitron and natron in late Latin were derived from the Arabic نطرون (Ntrun'), some of the vowels being usually omitted in writing that language as in shorthand. Similar difficulties occur with the terms in other languages. Nevertheless considerable progress has lately been made in ascertaining the early history of gunpowder and fire-arms, and various wild statements as to the great antiquity of the knowledge of gunpowder in some countries is now quite discredited, as it is found that the evidence upon which these statements were made will not bear scrutiny.

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Early Incendiary Mixtures.

Long before the discovery of saltpetre, incendiary materials had been used in warfare, such as pitch, sulphur, petroleum and other oils. Burning brands were frequently attached to arrows or were thrown by means of engines (catapults), and the descriptions of the effects produced by these early "fire-arms" is often so fanciful and exaggerated that they have been thought to imply the use of gunpowder, with which they really have no connexion. A ball of burning pitch mixed with sulphur and naphtha thrown against a wooden building or ship would cause a fire, which if not quickly extinguished might prove disastrous. Such incendiary mixtures were known in England as "wild-fire." The prompt application of a bucket of water or some sand would, however, remove the danger. Hence, although isolated instances occur in ancient history where great success was achieved with these incendiary mixtures, they must generally have proved ineffective.

Greek fire A.D. 668.

The one notable exception to this is the "Greek-fire" or "sea-fire," the secret of which prevented the conquest of Constantinople and Europe by the Moslems for several centuries. About the year A.D. 668, some forty-six years after the flight of Mohamed from Mecca to Medina, the Arabs, still at the height of their conquering enthusiasm, commenced to beleaguer Constantinople by land and sea, when an architect named Kallinikos fled from Heliopolis in Syria to the Imperial city and imparted the secret of the "sea-fire." This repeatedly spread such terror and destruction among the Moslem fleet, that it was the principal cause of the siege being eventually raised after seven years. In A.D. 716 to 718, the Arabs again appeared before Constantinople with eighteen hundred ships, but again were defeated by the fire; so effectually, that after a stormy passage only five galleys re-entered the port of Alexandria to relate the tale of their various and almost incredible disasters.

Russian naval forces were similarly defeated in 941 and 1043, and the Pisans at the end of the eleventh century.

What, then, was the nature of this "sea-fire"? It was discharged from tubes or siphons in the bows of the ships, but its mode of preparation was kept a close secret, and it was never used successfully by anyone but the rulers of the Eastern Roman Empire. Naphtha was probably an important ingredient of it. Colonel H. W. L. Hime came to the conclusion that it consisted of naphtha, quicklime, and sulphur.[1] The secret probably lay not so much in the names of the ingredients as in the exact method of compounding them and discharging the mixture.

Later the name "Greek fire" was given also to combustible materials which were ignited and then thrown by ballistæ or other machines, and were used on land, and this has led to some confusion. Thus Joinville, the faithful

A.D. 1250.

and devoted companion of St. Louis in the disastrous sixth Crusade (A.D. 1250), says that "it came flying through the air like a winged long-tailed dragon

[1] *Gunpowder and Ammunition*, London, 1904.

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about the thickness of a hogshead, with the report of thunder and the velocity of lightning; and the darkness of the night was dispelled by this deadly illumination." Nevertheless, the Greek fire on this occasion did very little damage. That men like St. Louis and Joinville, usually absolutely fearless, should have been terrified by such a cause and described it in such exaggerated language seems to have been due to the fact that they looked upon it as a product of the Devil. By 1250, however, the Arabs were acquainted with saltpetre, and it is quite likely that they mixed some with the incendiary, causing it to burn far more fiercely. Similar language is used in describing the incendiary missiles discharged by the Moors in Spain in battles and sieges of about the same date.

Saltpetre. Saltpetre (potassium nitrate) is formed in the decomposition of animal and vegetable matters. Under favourable conditions it forms an efflorescence on the ground. It must have been by the investigation of such efflorescences that saltpetre was first discovered. These efflorescences are never pure and seldom contain more than a small percentage of potassium nitrate. The ancients did not clearly distinguish such deposits of saltpetre from the similar ones of soda which are found in some localities. The first preparation of saltpetre of even moderate purity from such a deposit would require considerable chemical knowledge, and it could only have been done in a country where the deposits are plentiful, that is, in a country sufficiently warm to accelerate the decomposition of the organic matter and having a regular and prolonged dry season during which the deposit would collect and not be washed away. The climate of Western Europe is consequently not favourable, and moreover scientific knowledge and investigation were very backward in Europe in the early middle ages. The people who were most proficient in this branch of knowledge at that time were the Arabs or rather the Arabic-speaking people of Spain, Northern Africa and Syria, and many parts of these countries have climates suitable for the formation of saltpetre deposits. Consequently, it is not surprising that it is in Arabic that the first clear reference to saltpetre is to be found. This is in the writings of Abd Allah ibn al-Baythar, a Spanish Arab who died at Damascus in 1248. It seems probable that the Arabs and Egyptians knew saltpetre in a fairly pure state about 1225.

The Chinese. According to Romocki the Chinese were acquainted with it about the middle of the thirteenth century, but do not appear to have used it much at that early date. It is, however, possible that the Chinese were the original discoverers of saltpetre. The Egyptians called it "Chinese snow,"[1] and it is significant that Chingis, the Mogul conqueror, brought Chinese engineers with him in 1218 to reduce the fortifications of the cities of Persia.[2] The statements made by the early Jesuit fathers as to the great antiquity of the manufacture

1218.

[1] Hime, p. 17.

[2] Gibbon, chap. lxiv.

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of gunpowder in China, have been shown to be inaccurate and founded on erroneous translations.[1] Marco Polo, who was in the Far East from about 1274 to 1291, says concerning the city of Chan-Glu in Part II., Chapter L., of his book : " In this city and the district surrounding it they make great quantities of salt, by the following process ; in the country is found a salsuginous earth ; upon this when laid in heaps, they pour water, which in its passage through the mass imbibes the particles of salt, and is then collected in channels from whence it is conveyed to very wide pans not more than four inches deep. In these it is well boiled and then left to crystallize. The salt thus made is white and good, and is exported to various parts." The material prepared in this way could not fail to contain a considerable proportion of saltpetre, moreover the soil in the province of Che-li, in which the city mentioned seems to have been situated, is known to be rich in saltpetre. But from Marco Polo's statement it is probable that the product was used as common salt. In fact, the Chinese appear to have used saltpetre as ordinary salt even at much later periods.

The Indians

Statements have been made with regard to India upon similarly incorrect evidence. It is improbable that the refining of saltpetre can have been discovered in India, as the habits of mind of the educated classes would prevent their interesting themselves in such matters, and the institution of caste would render it impossible for them to handle many of the materials involved. But the same institution has enabled the saltpetre industry to be developed very widely, when once the process had been discovered elsewhere and introduced, as a special caste of saltpetre workers was formed, and India still supplies a large proportion of the saltpetre used. The saltpetre at first must have been very impure, as the methods of refining it were crude.

Roger Bacon 1214 to 1294.

Roger Bacon was perhaps one of the first men to obtain it in a fairly pure state. He must have been a man of great genius far in advance of his time, and much ahead even of the cleverest men of his own day. He disbelieved in magic and maintained that science and art could achieve greater wonders than those claimed for the Black Art. He wrote his *Epistola de Secretis Operibus Artis et Naturæ et de Nullitate Magiæ* to support this view. If the dedication of this work is authentic, it was written before 1249. The first eight chapters of this are quite clear and enumerate a number of wonders that may be accomplished by science. The ninth, tenth and eleventh chapters, however, appear at first glance to be nonsense, although some of the expressions in the eleventh seem to indicate that they contained instructions for the manufacture of gunpowder concealed by means of a cipher. His reason for hiding his meaning was that he considered knowledge injurious to the common people. In this he agreed with most of the ancients and the people of his own time, and in fact there are many at the present day who think

[1] Hime, chap. vii.

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the same. The invention of the first explosive was such a dangerous secret, that it is not to be wondered at that he did not think fit to divulge it to all. The fact that the ninth, tenth and eleventh chapters contain concealed secrets is confirmed by the fact that he repeatedly says he will use ciphers to hide his meaning, and in the eighth chapter enumerates seven ways in which it may be done ; namely, by using :

(1) Symbols and incantations (characteres et carmina) ;
(2) Enigmatic and figurative words ;
(3) Consonants only without vowels ;
(4) Letters from different alphabets ;
(5) Specially devised letters ;
(6) Pre-arranged geometrical figures ;
(7) Shorthand (ars notatoria).

As might be expected, the methods he has principally employed in the succeeding chapters are different from all these. After puzzling the world for many centuries they have been deciphered by Colonel H. W. L. Hime, who has given a clear and closely reasoned account of the whole matter in his book *Gunpowder and Ammunition.*

The passages in question profess to give the method of making the " philosophers' egg," but amongst many apparently meaningless sentences referring to chalk, cheese, gold and other things, are a number of words which when separated from the rest are found to be instructions for purifying saltpetre. This method is called the Argyle cipher and a good example of it is given in Thackeray's *Esmond.* Such a cipher could, of course, only be understood by a reader who knew what sort of information to expect, but the person to whom Bacon addressed the manuscript no doubt possessed the necessary knowledge.

Colonel Hime's translation of his solution of this part of the problem is as follows :

CHAPTER IX

" Carefully wash the natural saltpetre, and (as far as possible) remove all impurities. Dissolve it in water over a gentle fire, and boil it until the scum ceases to rise, and it is purified and clarified. Let the operation be repeated again and again, until the solution is clean and bright. Let it then deposit its crystals of the stone which is not stone,[1] and dry them in a warm place."

CHAPTER X

" Pulverize the crystals of grough saltpetre thus obtained, and immerse them in water. Make a powder of two purifying substances in the proportion 3 : 2. Dissolve the crystals over a gentle fire.

[1] *I.e.*, saltpetre.

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"To the powder add some animal charcoal [1] and thoroughly incorporate the ingredients. Then pour the hot solution upon it, and your object (of clarifying the liquid) will be gained.

"If the solution is good, pour it out. (While depositing crystals) stir the solution with a pestle. Collect the crystals as best you can and gradually draw off the mother liquor."

This method of refining salpetre does not differ very much from that followed in the gunpowder factories at Waltham Abbey and elsewhere in the second half of the nineteenth century. The principal differences are: that in the modern process after the concentrated solution has been boiled for some time and the scum removed, consisting partly of common salt, a little more water is added and the liquid is boiled up again, so that in cooling the sodium chloride may be kept in solution. Also the liquid is filtered before being allowed to crystallize. And finally the crystals of refined saltpetre are washed with water before drying.

The importance of refining saltpetre well lies not only in the fact that the impurities act as diluents, but they are hygroscopic and by absorbing water from the air make the saltpetre moist so that it will not act nearly so energetically. The property of saltpetre to aid the combustion of inflammable substances must have been well known to Bacon. Therefore he would try the effect of mixing his purer material with some of the substances usually used for incendiaries. On so doing he obtained an explosive and perhaps an unexpected explosion.

In Chapter XI, Bacon gives the composition of the explosive, but concealed one of the ingredients with even more care than before. The passage, which is of importance, is as follows:

"Item pondus totum 30 Sed tamen salis petræ *luru vopo vir can utriet* sulphuris; et sic facies tonitrum et coriscationem, si scias artificium. Videas tamen utrum loquor ænigmatate aut secundum veritatem." The part in italics had long been suspected to be an anagram concealing some word for charcoal, and many suggestions have been made for its solution. The only reasonable one is that of Hime, which is as follows:

r · VII Part · V nov · corul. V et,

or in full:

r(ecipe) VII part(es), V nov(ellæ) corul(i) V et.

Hime considers that Bacon's correspondent would have no difficulty in understanding "nov. corul." as meaning charcoal made from young hazelwood, as in a previous chapter he has referred to "virgulti coryli."

[1] The word in the original is Phœnice. As the Phœnix was said to rise anew from his own ashes, Hime has interpreted the word as a figurative term for animal charcoal.

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The translation of the passage is therefore :

" Let the total weight be 30, but of saltpetre take seven parts, five of hazel charcoal, and five of sulphur, and thus you will make thunder and a bright light, if you know the trick. You will see whether I am speaking riddles or telling the truth."

It must, however, be admitted that the matter is not yet quite free from doubt. For the anagram in the above form occurs only in printed editions of Bacon's work which were published at Paris in 1542 and Hamburg in 1618. In a manuscript preserved at Oxford, only the first six chapters are given. In another, in the British Museum,[1] the passage given above is the same except that the anagram is quite different. The dates of these manuscripts are not definitely known, and these passages may have been inserted later. Nevertheless the adversities of Roger Bacon's life are really quite enough to account for the unsatisfactory character of some parts of the writings that have come down to us from him.

In his *Opus Tertium*, written about the same time, a clearer passage has recently been found by Prof. P. Duhem in a fragment discovered in the Bibliothèque Nationale, Paris. The following free translation has been published by Colonel Hime in the journal of the Royal Artillery for July 1911 :

" From the flashing and flaming of certain igneous mixtures and the terror inspired by their noise wonderful consequences ensue. As a simple example may be mentioned the noise and flame generated by the powder, known in divers places, composed of saltpetre, charcoal and sulphur. When a quantity of this powder no bigger than a man's finger is wrapped up in a piece of parchment and ignited, it explodes with a blinding flash and a stunning noise. If a larger quantity were used, or if the case were made of some solid material, the explosion would of course be much more violent, and the flash and din altogether unbearable.

" If Greek fire, or any fire of the same species, be employed, nothing can resist the intensity of its combustion.

" These compositions may be used at any distance we please, so that the operators escape all hurt from them, while those against whom they are employed are suddenly filled with confusion."

That Bacon was acquainted with quite a powerful gunpowder mixture, and must, therefore, have had tolerably pure saltpetre, is shown by the following translation of a passage in the sixth chapter of *De Secretis*.

" There are other marvels of nature. We can produce in the air sounds like thunder and flashes greater than the worst terrors that nature produces. A small quantity of composition no bigger than one's thumb will give forth a deafening noise and a vivid flash."

[1] Sloane MS. 2156.

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Twenty years later in 1268, in his *Opus Magius*, Bacon again wrote: "Some (mixtures) make a terrible noise. . . . Thunder cannot be compared to it. Some are dreadful to see for they give a light far exceeding that of lightning. . . . We can try this in that child's toy[1] which is made in many parts of the world, although the appliance is only made to hold a quantity equal to a man's thumb, from the violence of that salt, which is called saltpetre, such a terrible sound proceeds in bursting of such a small thing made only of thin parchment that it seems to exceed that of thunder, and the brightness of the light is greater than that of any lightning."

There can be little doubt that soon after the discovery of saltpetre the Arabs introduced it into their "Greek fire" and other incendiaries. In Europe, saltpetre must have been more scarce than in Africa and Asia. Moreover, the chivalry of Western Europe looked upon such means of war with horror and perhaps were half aware that the use of them must eventually destroy their Order.

The Arabs.

In the *Liber Ignium* of Marcus Græcus, which was probably translated into Latin from an Arabic source about 1300,[2] there are several references to such mixtures, but the translator does not appear to have understood the subject he was writing on, and consequently it is not now possible to be sure whether he is endeavouring to describe fire brands, rockets or other fire-works. One "flying fire" (ignis volatilis) is composed of:

Resin	1
Sulphur	1
Saltpetre	2

dissolved in linseed oil and put into a (hollow) reed or piece of wood. This was evidently an incendiary (wild-fire).

Another is made of

Sulphur	1
Vine or willow charcoal	2
Saltpetre	6

These were rubbed down together on a marble slab and put into a case (tunica) in different manners according to the effect to be produced. To make a loud noise the case was to be short and wide, and filled only half full, and was to be bound with strong iron wire. Evidently this was a cracker not unlike that described by Bacon. On the other hand, the "flying tunica" was to be thin and long, and filled with the above powder well rammed in. This was evidently an imperfect rocket or squib. The same work contains a second description of these fire-works (recipes 12, 13, 32, 33), but this does not help to clear up the uncertainties.

[1] Perhaps a pea-shooter made of rolled parchment.

[2] *See* Hime, p. 103.

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That the Arabs were probably using saltpetre in their firebrands in 1250, is shown by the passage in Joinville, quoted above (page 4). At the siege of Niebla, in Spain, in 1257, we are told that the Moors "launched stones and darts from machines, and missiles of thunder and fire."

Chinese fire-works.

It has been stated by many, that the Chinese were acquainted with gun-powder and fire-arms in very early times. These statements were spread abroad by the Jesuit fathers, who in translating the old annals gave to words their modern meanings, whereas at the times the works were written they meant something quite different. When we come down to the year 1232, however, there is a statement of a different kind. In the chronicles called *Tung-Klan-Kang-mu* there is an account of the siege of Pien-King (now Kai-fung-fu) in 1232, and this was translated into French by Reinaud and Favé in the *Journal Asiatique* for October 1849 :

1232.

"At that time use was made of the 'ho-pao' or fire pao, called 'Tchin-tien-loui' or 'thunder that shakes the sky.' For this purpose an iron pot was used which was filled with 'yo.' As soon as a light was applied, the pao rose and fire spread in every direction. Its noise resembled that of thunder and could be heard more than 100 lis (thirty-three English miles) ; it could spread fire over more than a third of an acre. This fire even penetrated the breast plates on which it fell."

"The Mongols constructed with ox-hides a passage which enabled them to reach right to the foot of the rampart. They commenced to sap the walls, and made holes in them in which they could remain sheltered from the men above. One of the besieged proposed that they should hang fire-paos from iron chains and let them down the face of the wall. When they reached the places that were mined, the paos burst and shattered the enemies and the ox-hides, so as not to leave a vestige of them."

"In addition, the besieged had at their disposition some 'arrows of flying fire' (fei-ho-tiang) : to an arrow was attached a substance susceptible of taking fire ; the arrow flew suddenly in a straight line and spread flames over a width of ten paces. No one dared approach. The fire-paos and arrows of flying fire were much feared by the Mongols."

This arrow may have been a squib or a rocket, or merely an arrow to which a saltpetre mixture was attached. The effects described could hardly have been produced without the use of saltpetre, nor the great noise without an explosive, but we need not take literally the statement that it could be heard thirty-three miles away.

By A.D. 1259 the Chinese had made a further advance. The same annals state : "In the first year of the period Khai-King was made an appliance called 'tho-ho-tsiang,' that is to say, 'lance with violent fire.' A 'nest of grains' was introduced into a long bamboo tube, which was set light to. A

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violent flame came out and then the 'nest of grains' was shot forth with a noise like that of a pao, which could be heard at a distance of about 500 paces."

This was evidently the device now known as a Roman candle. The Chinese do not appear to have developed explosives beyond this point, or to have made the next step, namely, of causing the powder to throw a heavy projectile instead of a ball of fire. Perhaps they made the attempt, but with disastrous results to themselves.

This step could only be taken by a nation which was at once progressive and well acquainted with the working of metals. For some time the development of gunpowder must have been impeded by the scarcity and poor quality of saltpetre. Before any great advance could be made, it was necessary for a considerable organization to grow up for collecting the saltpetre and refining it. In the meantime all the available supply was no doubt absorbed by the makers of warlike combustibles.

In the thirteenth century, therefore, saltpetre was known and used from China to Spain and England, but before the invention of fire-arms its utility can have been but small. No reliable fuze having yet been discovered, hand grenades or bombs can have been of little use and must have been more dangerous to those using them than to the enemy. The fire-works which have been alluded to must have been very uncertain in their action and not without risk to the fire-worker. It does not seem to have occurred to anyone to use explosives to blow up the walls of a besieged town by mining underneath and firing off a large quantity; the primitive powder was no doubt too uncertain in its action and its properties were not well enough known. There is evidence to show that, for getting minerals, gunpowder was not used until the seventeenth century.[1]

Invention of firearms.

The real development of gunpowder and its extensive use had to wait, therefore, for the invention of the gun. It is generally considered that this was accomplished by the German monk Berthold Schwartz, as he is named as the inventor in many old manuscripts. There is, however, a curious inconsistency about the dates mentioned. The year 1380 is given by Flavius Blondus, Æneas Sylvius, Baptista Saccus and many others living in the fifteenth century. Other writers have stated that the invention was made in 1354, 1390, and 1393.[2] But on the other hand, there is no doubt that guns

1325.

were used much earlier. In an illuminated manuscript entitled *De officiis regum*, written by Walter de Millemete in 1325, and preserved in Christ Church Library, Oxford, there is a drawing of a rudimentary gun shaped like a bottle,

1331.

and discharging a dart. A man is applying a light to the touch-hole. In 1331 cannon were used by the Moors at the siege of Alicante.[3] In two

[1] *See* chap. ii.

[2] Guttmann, *Manufacture of Explosives*, 1895, vol. i., pp. 10–11.

[3] Utescher, *S.S.*, 1914, p. 100.

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frescoes in the church of the former monastery of St. Leonardo in Leccetto, near Siena, painted by Paolo del Maestro Neri in 1340 are shown a large cylindrical cannon discharging a spherical cannon ball, and many hand-guns.[1] 1340.

Artillery was apparently used by the Moors in the defence of Algeciras against Alfonso XI of Castille in 1342. The Counts of Derby and Salisbury were present with the Spaniards, and it is supposed that they introduced guns into England. In the following years there are several references in the accounts of the Wardrobe of Edward III of payments on account of saltpetre. Thus Thomas de Roldeston, Clerk of the King's Private Wardrobe in the Tower of London, gives an account for forty shillings for making powder and repairing various arms in the period 1344 to 1347 : " Eidem Thomæ super facturam pulveris per ingeniis et emendatione diversarum armaturam XL sol." [2] And an account was discovered by Guttmann delivered by John Cok, Clerk of the King's Great Wardrobe for the date May 10, 1346, for 912 lbs. of saltpetre, and 886 lbs. of quick sulphur for the King's guns : [3] " Et eidem Thomæ de Roldeston per manus Willielmi de Stanes ad opus ipsius Reis pro gunnis suis $\overset{c}{\text{I}}$ XXII lib. sal petræ et DCCC $\overset{xx}{\text{IIIIVI}}$ lib. sulphur vivi per breve Regis datum X die Maii dicto anno $\overset{o}{\text{XX}}$." When all possible allowance has been made for alterations in the meanings of words, there can be no doubt that in 1346 King Edward had guns and powder. On November 25, 1346, and again on September 21, 1347, an official order was given to buy all available saltpetre in the country. On the first occasion 750 lbs. of saltpetre and 310 lbs. of sulphur were obtained ; on the second, 2021 lbs. of saltpetre and 466 lbs. of sulphur. The price of the saltpetre was 18*d.* per lb., of the sulphur 8*d.* 1342. 1346.

At the battle of Crecy (August 26, 1346) guns were used by the English. The French are also believed to have possessed them, but apparently left them behind in order not to be encumbered with them in their pursuit of the English.

There was a powder mill at Augsburg in 1340, at Spandau in 1344 and Liegnitz in 1348.[4] Powder was, however, generally made in ordinary houses until repeated explosions showed the danger of doing so. There was a " powderhouse " in the Tower of London in 1461, and gunpowder was made inside the Tower for many years, as also in Porchester Castle. In 1555 there was a mill near Rotherhithe, and in 1561 we hear of mills at Long Ditton, Leigh Place near Godstone, Faversham and Waltham Abbey. Early powder mills, 1340–1348.

[1] *See* Guttmann, *Monumenta Pulveris Pyrii*, 1906.
[2] Guttmann, *Manufacture of Explosives*, vol. i., p. 13 ; Hunter, *Archæologia*, 1847, vol. xxxii.
[3] Public Record Office, London, L.T.R. Enrolled Wardrobe Account No. 4.
[4] Berthelot, *Revue des Deux Mondes*, August 15, 1891, p. 817.

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Summary. We see then that saltpetre became known about 1225 and that by 1350 fire-arms were in use to a considerable extent in Western Europe.

Saltpetre was apparently discovered by one of the Oriental nations, and was used for making fire-works and incendiary mixtures both in the East and West, but especially the East. The explosive properties of saltpetre mixtures must have been known to many people besides Roger Bacon, but they were of little use until the discovery of fire-arms, which apparently was made in Italy or Germany early in the fourteenth century.

The period of the first development of fire-arms was in many respects an important one. The division of the power in Italy, France and Germany among a great number of petty rulers had given the opportunity for the growth of the free cities on the one hand and the Papacy on the other. The latter had used its power to crush the Albigeois in Southern France, the most civilized and cultured people of the time, and by 1250 had extinguished them with fire and sword. The free cities were frequently richer than important countries, and it was in them that the skill and knowledge were developed which made it possible to construct ordnance and make gunpowder. Only in England did the king retain much power. In the East the prestige of Christianity and the "Franks" was then at its lowest ebb, but a steady advance was to come. The Christian religion had been extirpated from Africa and a great part of Spain, and in Syria the Crusaders had finally failed to retrieve the Holy Sepulchre. The Arabs had long since been obliged to resign most of their conquests to the Turks, who had reduced the Eastern Roman Empire to little more than the city of Constantinople, and that had become the spoil alternately of French, Normans, Venetians and Genoese. The final fall of the city was, however, postponed by the appearance of another race who came, like the Turks, from Central Asia. These were the Tartars or Moguls, the greatest conquerors known in human history. Under Chingis they conquered China in 1210 to 1214, Carizme, Transoxiana, and Persia in 1218 to 1224. The cities of the Middle East were reduced with the aid of a staff of skilful Chinese engineers, who perhaps brought with them the secret of saltpetre. Under the successors of Chingis fire and destruction were carried into Russia, Poland and Hungary. At the beginning of the fourteenth century the Mogul Empire declined under the civil wars which almost inevitably result on the death of a monarch in the East. The Turks regained their ascendancy for a time in Western Asia. In 1361 to 1405 Timour or Tamerlane usurped the whole of Chingis' Empire except China, and added to it Northern India, part of Syria and Asia Minor.

But already the forces were being born which were to revolutionize the world. In the cities of Italy, Germany, England and France a spirit of freedom in inquiry, adventure and culture was arising which now dominates the whole earth.

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NOTE.—The account of the Greek fire is largely derived from Gibbon's *Decline and Fall.* Although this remarkable work was written in the eighteenth century, yet such is its accuracy that even upon such a difficult and technical matter as this, subsequent research has been able to find no errors in the statements. In a footnote relating to the discovery of gunpowder, Gibbon says : Gibbon.

" The vanity, or envy of shaking the established property of fame, has tempted some moderns to carry gunpowder above the fourteenth and Greek fire above the seventh century. But their evidence, which precedes the vulgar æra of the invention, is seldom clear or satisfactory, and subsequent writers may be suspected of fraud or credulity. In the earliest sieges some combustibles of oil and sulphur have been used, and the Greek fire has *some* affinities with gunpowder both in nature and effects."

It is impossible to sum the matter up better.

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CHAPTER II

DEVELOPMENT OF GUNPOWDER UP TO THE END OF THE EIGHTEENTH CENTURY

Early powder-making machinery : Incorporating mills : Stamp-mills : Additions to gunpowder : Corned powder : Military mines : Projectiles : Incendiary missiles : Shell : Fuses : Grenades : Composition of gunpowder : Testing gunpowder : Sporting guns : Rifles : Fire-works : Blasting

Early powder-making machinery.

At first gunpowder was made by simply pounding up the constituents and mixing them together in a mortar. Often the pestle was suspended from a flexible wooden rod, which acted as a spring to assist the lifting. The earliest known example of such an appliance is shown in an illustrated manuscript, the "Codex Germanicus," preserved in Munich (No. 600 of the Hof- und Staatsbibliothek). Guttmann assigns to this the very early date of 1350.[1] Similar pictures appear in later manuscripts, such as the "Rust und feuerwerck buych" of the fifteenth century, in the Stadtbibliothek at Frankfurt a /M. The latter also shows the next step in the adoption of machinery, the stamp mill. Guttmann, in his *Monumenta Pulveris Pyrii*, gives reproductions of many old drawings of such plant. In the fifteenth and sixteenth centuries there were generally two stamps working in each mortar. They were raised alternately by a cam projecting from an axle which was turned by hand. At a later date water wheels and treadmills were used as the motive power, and only one stamp worked in each mortar. Horses do not seem to have been used.

Incorporating mill.

There is a picture of an incorporating mill with an edge-runner in a book entitled *Corona e Palma Militare di Arteglieria* by A. Capo Bianco, and published at Venice in 1598. It has only one edge-runner, and the machine is apparently turned by a horse working in the same building.

Stamp mills.

Stamp mills were still used extensively on the Continent at the end of the nineteenth century, but in England they were forbidden. Tilt hammers were also used sometimes, especially in Switzerland, and in more modern times rotating drums containing hard wood balls have been employed.

At first the powder was used in the fine state. In this condition it burned slowly, as the interstices were very small; it was liable to foul

[1] *Monumenta*, p. 19, Fig. 48.

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the fire-arm very badly after a few rounds, and it was difficult to regulate the effect, which depended very much upon the ramming. Bourne, in his *Art of Shooting in Great Ordnance*, 1587, said: "The powder rammed too hard and the wad also, it will be long before the piece goes off. . . . The powder too loose . . . will make the shotte to come short of the mark. . . . Put up the powder with the rammer head somewhat close, but beat it not too hard." Other disadvantages of the fine powder were that it absorbed moisture very rapidly, and the constituents were liable to separate one from the other if the powder were subjected to much vibration. For although amorphous carbon has much the same absolute density as saltpetre and sulphur, powdered charcoal contains many cavities which make it lighter than the other constituents.

Additions to gunpowder.

It was partly to prevent this separation of the constituents that the early powder-makers added camphor, sal ammoniac and gum dissolved in spirit to their powder. Thus in the "Codex Germanicus" of the fourteenth century the following recipe is given: "Wiltu ein gut starck pulver machen So nym IIII lb Salniter und I lb swebel und I lb kol/ I uncz salpetri und I uncz salarmaniak Item und ainen XII tail campfer und stoz daz alls wol undeinand/ und tu gepranten wein darczu und stoss damit ab. und derre daz wol an der sunn/ so hastu ein uberstarck beliwig pulver/ dez phunt mer tut denn sust III phunt getun möchten /und ist auch behaltig und wirt lenger pesser."

Translation: "If you want to make a good strong powder, take 4 lb. of saltpetre, 1 lb. of sulphur and 1 lb. of charcoal, 1 oz. of salpratica and 1 oz. of sal ammoniac and one-twelfth part of camphor. Pound it all well up together, and add spirit of wine and mix it in, and dry in the sun. Then you have a very strong powder, of which 1 lb. will do more than 3 lb. otherwise. It also keeps well and becomes better with time."

In another part of the same manuscript it is stated: "Wenn wa nicht gampfer pey ist daz pulver erwirt und verdirbt gern. Aber daz gamfer halt allez pulver auf/ und ist auch kreftig und prunstig in allem pulver wenn man in darin tut." Translation: "When there is no camphor, it crumbles and easily spoils. But the camphor holds all powder together, and is also strong and quick in all powder, if one puts it in."

"Salpratica" was a mixture of saltpetre, camphor and sal ammoniac, made by dissolving them all in spirit, placing the mixture in an unglazed earthenware vessel, and scraping off the efflorescence that was formed. The composition must have been very variable. These volatile materials were also supposed to improve the power of the explosive by increasing the amount of "air."

The separation of the ingredients was restrained at a later date by "corning" the powder, that is, breaking the cakes into small grains only, instead

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of to a fine powder. In order to get a hard mill-cake, which would give good grains, the contents of the mortar were moistened before the end of the stamping operation with water, wine or urine. After it had been broken down the grains of the required size were separated by sifting.

Corned powder. Corned powder burned much faster than the fine powder, which then came to be called "serpentine." The pressure it generated was too great for the big guns of that time, and its use was restricted to small-arms. Whitehorne, in his *Certain Waies for the Ordering of Souldiers in Battelray*, 1560, says: "If serpentine powder should be occupied (used) in handguns, it would scant be able to drive their pellets a quoit's cast from their mouths; and if handgun (*i.e.* corned) powder should be used in pieces of ordnance, without great discretion, it would quickly break or mar them."

According to Guttmann, the French powder-mills began in 1525 to grain and classify their powder by passing it through sieves.[1] Apparently corned powder came gradually into use for small-arms and hand-grenades during the fifteenth century, and for big guns in the sixteenth, the construction of these being sufficiently improved by that time. In an engraving by Phillip Galle, after a drawing by John Stradanus, to which the date 1570 has been assigned,[2] the operations of casting and finishing guns are shown, and the manufacture had evidently reached a fairly high state of development by that time.

Military mines. The same picture shows in the background the blowing up of a tower. Mines of gunpowder had, however, been used as early as 1415 by the English in the siege of Honfleur.[3]

Projectiles. The first projectiles used were made more or less like arrows with metal "feathers" and arrow-heads,[4] just as the first railway carriages were built like stage-coaches. These were soon found to be unsuitable and were replaced by round shot made of iron, bronze, lead or stone. All these materials remained in use for several centuries, but stone was the most common for large guns, partly because its cost was only a fraction of that of a metal shot of the same size, and partly because the guns would not stand the strain of discharging the heavier materials. Lead and iron bullets were usually used for small-arms, but in an emergency any small handy article was made use of.

Incendiary missiles. Attempts were made very early to throw from guns incendiary missiles such as had been discharged previously from machines, but some difficulty must have been experienced from the flames being extinguished by the rapid motion through the air. At the siege of Weissenburg in 1469 stone balls

[1] *Manufacture*, vol. i., p. 17. [2] *Monumenta*, Fig. 8.
[3] *Zschokke*, p. 10. *See also* A. Genez, *S.S.*, 1913, p. 396.
[4] *See Monumenta*, Plates 69, 70, 71; Hime, p. 199; *Rise and Progress*, Fig. 3.

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were used considerably smaller than the bore of the gun, and these were smeared over with incendiary matter and wrapped in a cloth soaked in the same mixture.[1]

Shell.

Actual shell could not be used at that time, because it was not known how to cast them in metal. But a sort of weak shell was made of earthenware, or by joining two hemispheres of metal. These were filled with a slow burning powder well rammed in, or other incendiary matter, and were provided with an igniter, which was set light to by the flame from the gunpowder of the propelling charge, but there must have been considerable uncertainty about the ignition, and of course it was much too dangerous to introduce a lighted shell into the bore of a gun which had been charged with serpentine powder by means of a shovel. The difficulty was sometimes overcome by enclosing the powder in a paper cartridge, but this method did not find general acceptance. Red-hot shot could not be used for the same reason, until Stephen Bathory, King of Poland, in 1579 used a thick wet wad to prevent the fire spreading to the charge. Hot shot were used with great effect in the defence of Gibraltar by the English in 1782.

Fuses.

For explosive shell the difficulty was to make a satisfactory igniter or fuse. The earliest record of really successful explosive shell is in the accounts of the sieges of Wachtendonck and Bergen-op-Zoom in 1588, the master gunner being an Italian refugee from Parma in the employment of the Dutch. The fuses used were apparently tubes or pipes filled with slow-burning powder, which were driven into the fuse-hole of the shell, and this type was adhered to until the middle of the nineteenth century and later, when concussion and percussion fuses were invented.

The fuses were made to burn 14 to 20 seconds, corresponding to ranges of 1000 to 2000 yards in the mortars, which were always used instead of ordinary guns for throwing shell. The shell were used for the destruction of stone fortifications and ships; against men they were not effective, as there was usually plenty of time to get away from them before they exploded. Until after the introduction of watches, which were invented by Huygens in 1674, no convenient means existed of testing the time of burning of a fuse. In the middle of the eighteenth century fuses were made of beechwood with a hole down the middle filled with fuse powder. The fuse could be cut to any required length. Great accuracy was not demanded of them, until Captain Mercier during the siege of Gibraltar in 1779 proposed to fire shell from guns instead of howitzers or mortars. Short "calculated" fuses were then used so as to make the shell burst over the Spanish working parties. The effect produced was considerable.

Accurate fuses were also required for the Shrapnel shell, which was devised by Lieutenant Shrapnel, R.A., about 1784, and officially adopted in 1803,

[1] Hime, p. 220.

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but they were made upon the same principle until the second half of the nineteenth century.

Hand-grenades.

Hand-grenades seem to have been used to a considerable extent in the first half of the sixteenth century, at which time they were probably made of earthenware. Whitehorne, writing in 1560, says that "earthen bottles or posses" had been formerly used, but he recommends "hollow balles of metal, as big as smal boules and ¼ in. thick, cast in mouldes and made of 3 partes of brasse and 1 of tinne." They were charged with "3 partes serpentine, 3 partes fine corne powder and 1 part rosen." A little fine corned powder was used as priming, and he directs that the grenades be "quickly thrown," as they will almost immediately "breake and flye into a thousand pieces."

In the seventeenth century the problem of the fuse for hand-grenades was fairly well solved, and regiments were formed of "Grenadiers," powerful men specially trained to throw grenades. Major Adye, writing in 1802, said they could be thrown twenty-six yards.[1]

Composition of gunpowder.

Colonel Hime gives the following Tables to show the alteration that took place in the composition of gunpowder in the course of time:

ENGLISH GUNPOWDER

Date	Authority	Saltpetre	Charcoal	Sulphur
1250	Roger Bacon	41·2	29·4	29·4
1350	Arderne (Laboratory receipt)	66·6	22·2	11·1
1560	Whitehorne	50·0	33·3	16·6
1647	Nye	66·6	16·6	16·6
1670	Sir J. Turner	71·4	14·3	14·3
1742	Robins	75·0	12·5	12·5
1781	Bishop Watson	75·0	15·0	10·0

FOREIGN GUNPOWDER

Date	Country	Saltpetre	Charcoal	Sulphur
14th Century	Germany	66·6	16·6	16·6
1560	Sweden	66·6	16·6	16·6
1595	Germany	52·2	26·1	21·7
1608	Denmark	68·3	23·2	8·5
1650	France	75·6	13·6	10·8
1697	Sweden	73·0	17·0	10·0
1882	Germany	78·0	19·0	3·0

[1] Hime, chap. x.

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The fourteenth-century German powder has been substituted for a French powder of about the same date mentioned by Hime, as it is a more satisfactory example. The last item in the list is German cocoa powder, ballistically the best "black" powder ever made.

But in reality the composition was extremely variable. Every powder-maker had his own formula in early days, and in the absence of testing apparatus there was no means of judging which was best. With the invention of corned powder another variable was introduced, the size of the grains, and the confusion became still worse.

In the Middle Ages the only tests applied to powder were to feel it to ascertain whether it was moist, and to burn a little to see whether much residue was left. The first instrument for testing powder, of which we have any knowledge, is that described by Bourne in his *Inventions and Devices*, published in 1578. It was a small metal cylinder with a heavy lid on a hinge. The lid was prevented from falling by a ratchet, and the angle to which it rose when powder was fired inside the box measured its strength. Testing gunpowder. 1578.

A much better instrument was that devised by Curtenbach and described by him in his *Halinitro Pyrobolia*, in 1627. This consisted of a heavy conical shot which rested on the mouth of a small mortar and could travel vertically upwards along a stretched wire. It was prevented from falling again by a series of catches. There is a copy of this in the Imperial Museum in Vienna, and Guttmann gives a reproduction of a photograph of it as Fig. 67 of *Monumenta Pulvis Pyrii*. 1627.

Master-Gunner Nye, in his *Art of Gunnery*, 1647, described the same instrument, and also proposed that the strength of powder be measured by firing bullets from a pistol into clay, or by firing a heavy ball from a mortar and finding out how far it travelled. This last, the *mortar éprouvette*, was adopted by the French and other Governments, and led to considerable improvements in the powders. By the beginning of the eighteenth century the proportions of the constituents were fairly well fixed, and the powders for different guns differed only in the size of grain. In 1742 Robins placed the matter on a more scientific basis by the invention of the ballistic pendulum, by means of which the actual velocity of a projectile could be measured. By the end of the century practically every country had come to use the proportions, 75 of saltpetre, 15 of charcoal, and 10 of sulphur. 1647.

Meantime fire-arms had gradually improved with the development of metallurgy and engineering skill. Chivalry had to acquiesce in the use of gunpowder in warfare, but made a longer struggle as regards the hunting of animals. Hawking and the chase were the only respectable forms of sport, but poachers were not governed by the same scruples, and laws were consequently passed to prevent the use of fire-arms by them. For instance, in

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1555 the Elector Augustus, of Saxony, prohibited the possession of fire-arms by peasants and shepherds, and in 1562 small shot was absolutely prohibited throughout the Duchy of Mecklenburg.[1] Nevertheless it was not possible to prevent the use of military muskets for sporting purposes. Italy, in this respect, as in so many others, was ahead of Northern Europe. Benvenuto Cellini (*b.* 1500, *d.* 1571) when a young man was very fond of shooting for sport, and made his own gunpowder. He shot with a single bullet and boasted of his skill as a marksman. He makes no mention of there being any prejudice or law against the use of fire-arms.[2]

Double-barrelled guns.

It was not until the double-barrelled gun was introduced that there was any real difference between the military and sporting weapons. Double guns were first made sufficiently light to be practicable in the middle of the seventeenth century; in the eighteenth century the ribs were added, and the flint lock and hammer were introduced.

Rifles.

Rifles were already known in the first half of the sixteenth century, and are said to have been invented by Augustus Kotter, of Nuremberg, in 1520, but for a long time the rifle was used principally for sporting purposes, because the necessity of ramming the bullet down the barrel with its spiral grooving made the loading very slow. Moreover, the powder left much fouling in the grooves, and consequently it was necessary to clean the arm after a few rounds. With the old musket, on the other hand, the bullet was smaller than the bore, and this trouble did not arise to anything like the same extent. In the seventeenth century the rifle was tried in several continental armies, but in every case it was given up again.[3] For sporting purposes accuracy was of more importance than rapidity of fire, and the rifle was able to hold its own, especially in mountainous countries such as the Tyrol and Switzerland. In the American War of Independence the sporting rifle was necessarily used for military purposes, and the English Government found it advisable to enlist on the Continent a corps of "Jägers" to put against the colonial marksmen. Afterwards the Rifle Brigade was raised, and this proved a success from the first. Robins, the inventor of the ballistic pendulum, had already prophesied that wonderful effects would be produced by the State which could first make the military rifle a practical success.

Fire-works.

Fire-works seem to have been made soon after the discovery of gunpowder: references to them are found in the writings of Hassan-er-Rammah, Roger Bacon, Marcus Græcus, and Albertus Magnus in the thirteenth and fourteenth centuries. The essential features were developed early, and later centuries have added nothing really novel. Improvements have been made in the artistic effects, precision of execution and safety, but the general principles are the same. The introduction of chlorates at the end of the eighteenth

[1] Greener, *Modern Shot Guns*, 2nd ed., p. 1.
[2] *Vita di Benvenuto Cellini*, part i.
[3] *Textbook of Small-Arms*, 1909, pp. 6, 7.

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century has been of some assistance, but their use has been restricted on account of the dangerous character of many chlorate mixtures. In the seventeenth and eighteenth centuries large sums were spent in Europe on fire-work displays to celebrate special events, but they were not much used in war. Carcasses containing incendiary composition, smoke-balls and light balls were used, however, in the Peninsula.[1] The Indians fired rockets in the defence of Seringapatam in 1792, but they do not appear to have done much damage. At the siege of the same town in 1799 explosive rockets seem to have been used with some effect.[2] Soon after this the Ordnance Office applied to the Royal Laboratory, Woolwich, for the services of some one who understood the manufacture of rockets. The Laboratory referred the Ordnance Office to the East India Company, who replied that they knew of no one who possessed such knowledge.

Colonel Congreve of the Hanoverian Army (afterwards Sir W. Congreve) was thus led to make experiments, and he devised the Congreve rocket, the most powerful thing of the kind that had been used in warfare. It proved very effective at Copenhagen and Walcheren in 1807, and at the passage of the Adour in 1813, but it was at the battle of Leipsic that it achieved the greatest renown, for a French infantry brigade in the village of Paunsdorf, unable to withstand their well-directed fire, surrendered there to the Rocket Brigade. At Waterloo also good service was rendered.

Since the Napoleonic wars the improvements in ordnance have been so great that the war rocket is no longer used. For military purposes rockets are only fired now as signals and to illuminate the enemy's position at night, and for the latter purpose they have been displaced to a great extent by star shell.

Blasting

For blasting minerals gunpowder does not appear to have been used until the seventeenth century. The first recorded blasts were made by Gaspar Weindl at Schemnitz, in Hungary, and from there the method was introduced into Germany in 1627. In 1689 Thomas Epsly Senior, started the use of gunpowder in the Cornish mines.[3] The late Mr. Oscar Guttmann, in his book on *Blasting*, published in 1906, gave the following concise account of the further progress :

"When bore-holes first came into use they were made with iron-mouthed borers, fairly large—nearly 3 inches in diameter, and then closed with a wooden plug, termed the 'shooting plug.'

"Henning Hutman in 1683 employed a kind of drilling-machine. In 1685 clay tampings, and in 1686 firing-tubes, began to be used. In 1689 paper cartridge cases were used to replace the older form of leather, and in 1717 bore-holes of smaller diameter came into vogue. The use of the chisel-

[1] *Rise and Progress*, p. 174. [2] Hime, p. 129. [3] Feldhaus, *S.S.*, 1908, p. 218.

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borer dates from 1749, blasting the untouched breast from 1767 (first at Zinnwald)."

It is only by blasting operations that many of the engineering feats of modern times have been made possible. In constructing means of communication, such as roads, canals and railways, immense quantities of explosives have been used.

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CHAPTER III

PROGRESS OF EXPLOSIVES IN THE EIGHTEENTH AND NINETEENTH CENTURIES

Berthollet, Chlorate : Igniters : Forsyth's detonator lock : Fulminates : Caps : Fuses : Gun-cotton : Nitro-glycerine : Ammonium nitrate explosives : Sprengel explosives : Coal-mine dangers : Cheddite : Inspection of explosives : Smokeless powders : Picric acid

In the nineteenth century commenced the active application of science to explosives, with the result that this industry like so many others developed enormously. In this chapter no attempt will be made to give in detail the history of each invention ; only the principal discoveries will be mentioned, and an attempt will be made to show how one has led up to and assisted another.

When chemistry was put on a firm basis at the end of the eighteenth century, there was a great increase in the number of chemical compounds which could be made in the laboratory. No man had more influence upon chemical science than Count Claude L. Berthollet (1748–1822). Amongst the substances which he discovered was potassium chlorate, or at least he in 1786 first showed clearly how it could be prepared in the pure state, and he investigated and described its properties ; for it seems to have been known to Glauber (1603–1668). Berthollet found that potassium chlorate, if substituted for saltpetre, produced a more powerful (or violent) explosive, and proposed in 1788 to manufacture gunpowder with it. But the results were most disastrous. A party had been made up to see the first of the new powder made in the mills : M. and Mme. Lavoisier, M. Berthollet, the Commissary, M. de Chevraud and his daughter, the engineer, M. Lefort, and others. Whilst the mixture was being incorporated in a stamp-mill the party went to breakfast. Lefort and Mlle. de Chevraud were the first to return, and as they did so the charge exploded with great violence, throwing them to a great distance and causing them such injuries that they both died in a few minutes. **Berthollet, chlorate.**

In spite of repeated attempts it has not been found possible to make a satisfactory propulsive explosive with chlorate ; the explosion is always liable to be too violent and uncontrollable. But another use in connexion with explosives was soon found, namely, for igniting gunpowder.

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Igniters. The first fire-arms were set off by means of a lighted match, which was applied to a priming of fine powder. Rain or wind seriously interfered with the operation. In the eighteenth century the flint lock was devised and a lighted match was no longer necessary. In its best form the priming powder was contained in a small chamber which was uncovered only at the instant when the descending flint struck a spark from the steel. Although this was a great improvement it left much to be desired as regards ease of loading, rapidity of ignition, and fouling of the touch-hole. Hence the persevering attempts to devise an easier and simpler method.

Forsyth's detonator lock. In 1805 the Rev. A. J. Forsyth, a Scotch minister, made a sporting gun with a detonator lock, and in the next year submitted his invention to the Master-General of Ordnance, who asked him to adapt it to the requirements of the Service. Forsyth's device consisted of a receptacle or magazine shaped like a scent-bottle, which was attached to the lock of the gun. It contained a detonating mixture of potassium chlorate, charcoal and sulphur. By rotating the magazine a small quantity of this was caused to fall into a small hole in a plug communicating with the touch-hole of the gun, and on again rotating the magazine it was brought into such a position that the portion of detonating priming could be set off by the fall of the hammer.

Forsyth spent some £600 in trying to produce a satisfactory device for military purposes, and he claimed to have succeeded, but the Government authorities were not convinced and did not adopt it. At the time they only paid Forsyth's expenses, but they granted £1000 to his relatives shortly after his death.

For sporting purposes Forsyth's invention had some success, but the profits must have been largely swallowed up by the numerous lawsuits that he instituted to protect it from 1811 to 1819. Before very many years had elapsed Forsyth's device was displaced by the copper tube or cap, containing fulminate of mercury.

Fulminates. Fulminates of gold and silver have long been known. Pepys, in his diary for November 11, 1663, recounts a conversation with a Dr. Allen, who told him about *Aurum fulminans*, 'of which a grain . . . put in a silver spoon and fired, will give a blow like a musquett and strike a hole through the silver spoon downward, without the least force upward."

Mercury fulminate. The fulminates of gold and silver are, however, too sensitive and dangerous for any practical use, but they have played their part as toys and scientific curiosities. Liebig, who was born in 1803, when a boy saw a quack in the market-place of Darmstadt make fulminating silver. The alcohol he recognized from the smell of a garment which the quack had cleaned with liquid from the same bottle. He went home and succeeded in making the substance. In 1823, when he was in Paris with Gay Lussac, he investigated the fulminates at the suggestion of the latter, and isolated fulminic acid. By that time the

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comparatively stable fulminate of mercury was well known, having been described by Edward Howard, F.R.S., in a paper before the Royal Society in 1800. It is stated that it was manufactured in France in 1819.

Fulminate cap.

There is some uncertainty as to who first invented the fulminate of mercury cap, but it seems that several people were working at the idea at the same time and contributed towards the final success. According to H. Wilkinson,[1] J. Shaw, of Philadelphia, invented a steel cap in 1814; in 1815 a pewter cap, and in 1816 a copper cap. The London gun-maker, Joseph Egg, seems to have adopted the idea from Shaw. The Paris gun-makers, Prélat and Deboubert, in 1820 patented caps filled with fulminates of silver and mercury respectively. E. Goode Wright, of Hereford, in 1823 published a paper[2] on the fulminate of mercury cap, and subsequent workers seem to have derived much information from it. Frederick Joyce was the first to make a real success of the percussion cap about 1824. The firm of Joyce and Co. claim an earlier date, but although experiments may have been made in previous years there appears to be no evidence of manufacture on a considerable scale.[3]

The capped cartridge.

The next important step was to combine shot, powder and cap in one cartridge, which could be inserted in the breech of the arm. Many attempts had been made from very early times to make breech-loading fire-arms, but workmanship and knowledge of engineering were not sufficiently advanced to make a success of it. In 1836 Lefaucheux introduced his pin-fire breech-loading shot-gun, the barrels of which were made to drop as in the modern shot-gun to allow the cartridges to be introduced. This gun, although it had many imperfections, combined all the principal features of those made at the present day. About 1853 the English and French gun-makers introduced the central fire hammer gun, which fired cartridges having a cap in the middle of the base of the cartridges, but the first really successful central fire gun was that made by Daw in 1861.[4]

Breech-loading rifle.

In 1841 the Prussians adopted a breech-loading rifle, the "Zündnagel-gewehr," invented in 1838 by Dreyse. In this ignition was effected by a needle being driven right through the base of the cartridge into a disc of fulminating material. After a few rounds the rifle could not be fired from the shoulder in consequence of the escape of flame. The needles also rusted and broke. But in spite of its defects the gain in rapidity of fire caused it to be maintained as the general arm in the wars of 1848, 1866, and 1870.[5]

Chassepot rifle.

The French adopted the Chassepôt in 1866. This was a considerable improvement upon the Prussian rifle; escape of gas at the breech was

[1] *Engines of War*, p. 187.

[2] *Phil. Mag.*, vol. lxii., p. 203.

[3] The account of the discovery of the percussion cap is largely taken from the paper by E. Wyndham Hulme, B.A., in the *Rise and Progress of the British Explosives Industry*, London, 1909. *See also* Utescher, *S.S.*, 1914, p. 101.

[4] Greener, *Modern Shot Guns*, 2nd ed., 1891, p. 4.

[5] *Textbook of Small-Arms*, 1909, chap. ii.

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prevented by means of a rubber washer. About the same time a committee sat in England to decide upon a rifle, and finally selected that of Mr. Jacob Snider, an American. But at the suggestion of Colonel Boxer the cartridge case was made of brass instead of thin paper as in previous rifles. This not only greatly improved the accuracy of shooting, but effectually prevented the escape of gas at the breech.[1]

Safety fuse.

The old method of firing a blasting charge was to lay a train of powder up to it, or use a quill or rush filled with powder. The time taken by these to burn was very uncertain, however, and this caused numerous accidents in the mines. This led Mr. William Bickford, of Tuckingmill, Cornwall, in 1831 to devise his "miner's safety-fuse," wherein a continuous thin core of powder was contained in cable of jute and string.[2] This gradually came more and more into use, and the fuse was improved in quality as experience was gained in its manufacture. For use in wet places a special quality was made covered with tape and varnished. Soon after 1840 the Bickford fuse was adopted by the English military authorities. In 1836 a factory was started in America; in 1839 in France, and in 1844 in Germany. Before 1840 gutta-percha-covered fuse had been adopted for blasting under water. Various modifications have since been invented, including fuse cased in metal, "Colliery Fuse," which emits no sparks,[3] and various sorts of "instantaneous fuse," which burn very rapidly and enable many shots to be fired simultaneously.

Shell fuses.

As stated in the last chapter the fuses of shell were originally arranged to be ignited by the flash of the powder charge in the gun. The invention of the percussion cap, however, made it possible to start the action of the fuse in another and more certain manner. In 1846 Quartermaster Freeburn, R.A., invented the first English time fuse started by the concussion of the discharge; and in 1850 Commander Moorsom, R.N., brought forward the first percussion fuse which was actuated by the shock of impact of the shell.[4] These two types of fuse are still in use and are made to screw into either the nose or base of the shell. Very often both methods are combined in a "time and percussion fuse."

Gun-cotton. 1846.

Gun-cotton was discovered in 1845–1846 by C. F. Schönbein, Professor of Chemistry at Basle, in the course of some experiments which he was making upon highly oxidized bodies, following up a train of thought suggested by his discovery of ozone in 1844. Pélouze had made an explosive in 1838 by the action of nitric acid on cotton, but he did not take the important step of mixing sulphuric with the nitric acid, and he did not make any practicable application of his explosive. Schönbein at once recognized its importance as an explosive and kept the method of preparation secret, whilst he endeavoured

[1] *Text-Book of Small-Arms*, 1909.
[2] Eng. Pat. No. 6159 of 1831.
[3] Patented by Sir G. Smith in 1886.
[4] Hime, p. 245.

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to sell the process to various Governments. He showed that when fired in a musket gun-cotton produced the same velocity as a much greater weight of gunpowder. Professor Böttger, of Frankfort-on-Main, discovered gun-cotton in 1846, independently of Schönbein, but he entered into an arrangement with him to share the profits of the invention. Several others, attracted by the great stir that was caused by the invention, endeavoured to make gun-cotton, and some of them succeeded, but Schönbein was able to maintain the start he had obtained. In the autumn of 1846 he came over to England and gave some very successful demonstrations at Woolwich and Portsmouth and before the British Association. In the name of John Taylor he took out a British Patent,[1] and he entered into an agreement for three years with John Hall and Sons that they should have the sole right to manufacture gun-cotton at their powder works at Faversham, and in return should pay one-third of the net profit with a minimum of £1000 down, and the same each year. But before a year had elapsed, on July 14, 1847, there was an explosion of the gun-cotton which destroyed the factory and killed twenty-one men. After this Hall and Sons refused to proceed with the manufacture. About the same time there were disastrous gun-cotton explosions at Vincennes and Bouchet, and these produced such an effect that no more gun-cotton was manufactured in England or France for some sixteen years.

Meantime Schönbein had offered his process to the German Union (Deutscher Bund) for 100,000 thalers, and a committee had been formed to consider the matter, on which Liebig represented the state of Hesse, and Baron von Lenk, who was secretary, represented Austria. This committee sat until 1852, but finally refused to buy the process, partly on political grounds. The individual members of the Union were then able to make separate negotiations, and at the suggestion of von Lenk, who had done most of the actual work of the committee, Austria acquired the process for 30,000 gulden.

In 1852 the Emperor of Austria appointed a committee to inquire into the use of gun-cotton for military purposes, and with some interruptions this continued to sit until 1865. In 1853 a factory was erected at Hirtenberg to carry out von Lenk's method of making gun-cotton. In this the purification was somewhat more thorough than in Schönbein's original process, for instead of merely washing with water until neutral, von Lenk washed for three weeks, then boiled with dilute potash solution for fifteen minutes, washed again for several days, impregnated the yarn with water-glass, and finally dried. Von Lenk also constructed some batteries of 12-pounder guns to be fired with gun-cotton cartridges. These guns were so much damaged by firing, however, that no other nations adopted them. About 1860 von Lenk introduced bronze guns, which were less liable to burst than iron ones, and these not only had a propulsive charge of gun-cotton, but also had shells

von Lenk.

[1] No. 11407, October 8, 1846.

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containing a bursting charge of the same explosive. It was found, however, that these often burst in the bore, and this was evidently due to the very sudden shock of the discharge exploding the shell charge, for when gunpowder was used to fire the gun-cotton shells, no bursts took place. On July 30, 1862, the magazine at Hirtenberg exploded, and this seems to have finally decided the Austrian authorities to give up gun-cotton as a propulsive explosive, and von Lenk was then allowed to communicate the method of manufacture to other Powers. In 1865 another magazine exploded on Steinfelder Heath, near Vienna, and on October 11, 1865, the manufacture was officially stopped in Austria.

The further development then took place in other countries. Von Lenk made communications to the Emperor Napoleon III, and experiments were started in France. In 1864 he took out an American patent.

In 1862 and 1863 von Lenk took out patents in England in the name of Révy to protect his methods of purification,[1] and in the latter year he came over with the permission of the Emperor to describe his process to a com-
1863. mittee of the British Association. The same year Messrs. Prentice and Co. started to make gun-cotton at Stowmarket by von Lenk's process, but an explosion occurred there soon after.

Abel. Under the direction of Frederick Abel, the Chemist of the English War Department, manufacture was also started about the same time on a small scale in the Royal Gunpowder Factory at Waltham Abbey. This made it possible for Abel to carry out those experiments and researches which led to a revolution in the explosives industry, and have rendered gun-cotton one of the safest explosives in manufacture and use. In 1865 he took out a patent for pulping gun-cotton and pressing it into blocks,[2] and in 1866 and 1867 he published his *Researches on Gun-cotton*.[3] He showed that by pulping gun-cotton in the same way as is done with rags, &c., in the manufacture of paper, he not only got it in a more convenient state for pressing into blocks, but the violent mechanical treatment removed much of the impurity, and the gun-cotton was reduced to a condition in which it was much easier to wash it thoroughly. The object of compressing the pulped gun-cotton was to restrain the violence with which it exploded in the gun,[4] but although it was better than von Lenk's yarn it was still uncontrollable; it damaged the guns, and the accuracy of the shooting was unsatisfactory. It was not until some seventeen years later that a successful smokeless military powder was made. Gun-cotton was therefore only used for blasting purposes. Prentice

[1] Eng. Pats. 1090 of 1862 and 2720 of 1863.

[2] Eng. Pat. No. 1102 of 1865. The pulping of gun-cotton had, however, been carried out at Le Bouchet in France (*see* Escales, *Schiessbaumwolle*, 1905, p. 15).

[3] *Phil. Trans. of Royal Society*, 1866, p. 269; and 1867, p. 181.

[4] *See Chem. News*, 1866, (4) p. 250, and 1871, (24,) p. 141.

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and Co., of Stowmarket, adopted Abel's process of purification and have continued to use it ever since. In 1868 its utility was much increased by the discovery by Abel's assistant, E. A. Brown,[1] that dry compressed gun-cotton could be caused to explode very violently by a detonator containing fulminate of mercury, this appliance having been already used by Nobel [2] for detonating nitro-glycerine. Brown afterwards made the further discovery that a slab of wet gun-cotton could be exploded by means of a small primer of dry gun-cotton. This rendered it possible to store the greater part of the gun-cotton in the wet state, a great advantage for military purposes, and in this field gun-cotton as originally prepared under the superintendence of Abel still holds its ground to some extent.

Nitro-glycerine.

In 1846 nitro-glycerine was discovered by Sobrero, Professor of Chemistry at Turin, who had been assistant to Pélouze in 1838 when he made his first experiments on nitrating various bodies. But no practical application was made of it except that very small quantities were used in medicine as a cure for angina pectoris. People were no doubt deterred by the dangerous nature of the material and the inconvenience of dealing with a liquid explosive, as also by the difficulty in causing it to explode. In 1859 to 1861, however, Alfred Nobel and his father made experiments with it, and found that it could be exploded by means of a detonator containing fulminate, and in 1862 commenced to manufacture it at Heleneborg, near Stockholm. Many serious accidents occurred in the transport and use of the explosive, and in 1864 an explosion took place at the Heleneborg works, which destroyed them, killed the head chemist and Nobel's brother, and caused his father a paralytic stroke from which he never recovered. Nobel, however, was not deterred by this, and proceeded to re-erect his factory at Vintervikken, and build a new one at Krümmel in Germany. He was convinced that nitro-glycerine was the most powerful explosive known or likely to be discovered, and he allowed nothing to prevent him turning its properties to profitable account. The continual catastrophes, however, caused the various states to pass laws restricting or prohibiting the transport and use of nitro-glycerine. In consequence Nobel searched for means to make the material safer and more convenient to handle, and discovered that kieselguhr had the power to absorb three times its weight of nitro-glycerine.[3] This, combined with the fulminate detonator mentioned in the same specification, produced a very convenient and fairly safe explosive. Nobel then proceeded to exploit his inventions, and he did this with such success that by 1873 fifteen factories had been built or founded in the various countries of Europe and America. In 1875 he made another important invention,[4] that of blasting gelatine. The nitro-glycerine in this explosive was solidified by having about 8 per cent. of collodion cotton

[1] Eng. Pat. No. 3115 of 1868.
[2] Eng. Pat. No. 1345 of 1867.
[3] Eng. Pat. No. 1345 of 1867.
[4] Eng. Pat. No. 4179 of 1875.

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dissolved in it. As compared with kieselguhr dynamite this has two advantages: the nitro-glycerine is not liable to be displaced from it by water, a defect which in the case of dynamite has led to many accidents; and, secondly, the substance added is itself an explosive, and consequently blasting gelatine is 25 per cent. more powerful than dynamite. Gelatinized nitro-glycerine containing a small proportion of collodion has been made a constituent of many blasting explosives, the nature of the other constituents and the method of preparation being modified to produce explosives suitable for blasting different sorts of rock and other materials.[1]

Ammonium nitrate explosives.

In 1867 the Swedish chemists, C. J. Ohlsson and J. H. Norrbin, took out a patent for explosives consisting of ammonium nitrate, either by itself or in admixture with other substances such as charcoal, sawdust, naphthalene, picric acid, nitro-glycerine or nitro-benzene. They were led to their invention by theoretical calculations, which showed that a very large amount of heat and gas was given off in the explosion of these mixtures. They selected the proportions so that all the carbon should be converted to carbon dioxide and the hydrogen to water. Considerable difficulty was, however, experienced in igniting the charges, and consequently they usually added some nitro-glycerine to assist the explosion. Afterwards they used the fulminate detonator. The explosive was used to some extent in Sweden. Early in the seventies Alfred Nobel bought up the invention and took out further patents in connexion with it, but great difficulties were experienced in consequence of the very hygroscopic nature of ammonium nitrate. Soon after this Nobel invented blasting gelatine, and he did not take much active interest in ammonium nitrate explosives for some time.

Sprengel explosives.

In 1871 Dr. Hermann Sprengel, F.R.S., the celebrated inventor of the mercury vacuum pump, took out patents for a whole series of mining explosives to be made by mixing an oxidizing substance with a combustible one[2] "in such proportions that their mutual oxidation and de-oxidation should be theoretically complete." The essential feature was that the two constituents were to be mixed together on the spot just before the explosive was required, and the mixture was to be exploded by means of a fulminate detonator. As oxidizing agents he mentions amongst others nitric acid and chlorate of potash; as combustibles, a very large number of substances including nitro-benzene, nitro-naphthalene, carbon bisulphide, petroleum, picric acid. Liquid nitric acid is a most objectionable material to handle, nevertheless several inventors have taken out patents for Sprengel explosives containing nitric acid either enclosed in glass tubes or absorbed in fossil flour or other

[1] A very interesting account of Alfred Nobel and his inventions was contributed by de Mosenthal to the *J.S.C.I.* for 1899, p. 443.

[2] Brit. Pats. Nos. 921 and 2642 of 1871. *Journal of Chem. Soc.*, August and September 1873.

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similar material.[1] Needless to say, they have never found favour. In addition to its other disadvantage there is the serious danger that the nitric acid may come in contact with the detonator and cause a premature explosion. This actually happened in 1884 to the inventor Punshon.

Sprengel explosives consisting of chlorate of potash and a liquid combustible material have, however, been used to a considerable extent. The American, S. R. Divine, took out a patent in 1880 for mixtures of this sort and several English patents in the following years.[2] One of these mixtures, under the name of Rackarock, was used on October 10, 1885, for the great blasting operation of Hell Gate in New York Harbour. On this occasion 240,399 lb. of Rackarock were used together with 42,331 lb. of dynamite.

There are considerable advantages in transporting separately two such inert substances as nitro-benzene and chlorate of potash, but against this must be put the difficulty and inconvenience of mixing the constituents in the right proportions on the spot. If made up beforehand the cartridges are dangerously sensitive and become more so on keeping. Under the English Explosives Act this mixing is considered to constitute the manufacture of an explosive, and consequently may only be carried out in a duly licensed factory. Therefore Sprengel explosives have never been used in the British Isles, but they were introduced by the Americans into China and Siberia when the first railways were built there, and one of them is now licensed in Italy.[3]

Oxyliquit.

A somewhat similar explosive Oxyliquit, invented by Linde, consisted of liquid oxygen absorbed in wadding, charcoal, or other organic material. It was found that these mixtures would not detonate readily, so kieselguhr was substituted as absorbent with an addition of liquid petroleum. This detonated all right, but was more sensitive to a blow or spark than dynamite. It was very inconvenient to use, as the cartridge had to be fired within five or fifteen minutes of its preparation, according to the diameter. The explosive was tried in 1899 by a commission in Austria, and on a fairly large scale in the building of the Simplon tunnel, but in spite of the low cost of liquid oxygen it was found that the practical difficulties were too great.

Picric acid.

Sprengel also drew attention to the fact that picric acid by itself could be detonated by a powerful detonator and was a very violent explosive. No use was made of it in this way until many years later.

Coal-mine dangers.

The revival of ammonium nitrate explosives was due to the demand for such as would not ignite the fire-damp in coal-mines. Numerous disasters due to the explosion of fire-damp led to the appointment of commissions in

[1] Hellhoff, Brit. Pats. 1315 of 1879, 1285–87 and 2775 of 1880. Punshon, Brit. Pats. 2242 of 1880, 2428 of 1883. Bichel, French Pat. 171,169 of 1885.

[2] Eng. Pat. Nos. 5584 and 5596 of 1881, 1461 of 1882, 5624–25 of 1883.

[3] Guttmann, *Twenty Years Progress*, p. 10.

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many of the countries of Europe to inquire into the matter and propose remedies. The nature of the danger was investigated in 1815 by Sir Humphry Davy, and one source of disaster was removed by the substitution of the Davy lamp for the naked light. As time went on gunpowder was used more and more for breaking the coal, and after 1870 dynamite was also used. About 1873 Macnab proposed to insert a cylinder filled with water in front of the charge. Others have suggested wet moss, jelly containing 90 per cent. water and sawdust saturated with a solution of alum and sal ammoniac. But these devices were found to be cumbersome and expensive and not very effective.

Marcelin Berthelot.

In 1870, during the Siege of Paris, Professor M. Berthelot, who had hitherto devoted himself to pure science, was called upon to give his city and country the benefit of his scientific knowledge, and he was thus led to study the subject of explosives and especially to consider the amount of heat or energy liberated in the reactions which take place, for he had been working at thermo-chemistry for some years and was practically the founder of this branch of science. After the war was over Berthelot's services were still retained by the State in connexion with all matters connected with explosives. On the recommendation of the French Academy of Sciences he was in 1876 appointed a member of the Committee on "Poudres et Salpêtres." In order to deal adequately with the many new inventions he recommended the formation of a special commission. This was done in 1878, and Berthelot was appointed president of the new "Commission des Substances explosives," a position which he occupied for many years.

In 1877 a commission was appointed in France to inquire into the question of ignitions of coal-damp. In the report which it made in 1880 it was obliged to admit that there was then no explosive known that would not ignite coal-damp. An English Commission which reported in 1886 was forced to come to an equally unsatisfactory conclusion.

Prussia.

In 1885 the Prussian Government built at Neunkirchen the first testing station for investigating mining explosives and adopted a method of testing, which with slight modifications has been copied by the Governments of England and several other nations. A long iron cylinder was filled with mixtures of coal-damp, coal dust and air, and the explosives were fired. At first the explosive was simply suspended in the gas mixture, and it was found that the gas was ignited every time. Afterwards it was fired from a small mortar without tamping, and it was found that under these conditions kieselguhr dynamite was safe up to 100 grammes, and gelatine dynamite up to about 80.

1886-87.

It was now that ammonium nitrate explosives came to the fore again, as experience showed that considerably larger charges could be used without igniting the gaseous mixture. Two of the first of these were roburite and securite, mixtures of ammonium nitrate with dinitro-benzene. But it was

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also found possible by suitable admixtures so to alter the character of nitro-glycerine explosives that they can be used in coal-mines with comparative safety. In 1885 Schmidt and Bichel introduced carbonite, a mixture of nitro-glycerine, saltpetre and flour. This has been able to hold its own to the present day and is still considered one of the best safety explosives.

France. In 1887 another commission was appointed in France to inquire into the matter. Influenced by Berthelot's work and theories it directed its attention mainly to the question of the heat developed by an explosive and the resulting temperature of the products. Explosives having a high temperature of explosion, such as nitro-glycerine (3200°), gun-cotton (2600°) or collodion cotton (2060°), should be mixed with a substance having a low temperature of explosion such as ammonium nitrate (1130°). Three sorts of safety explosives were therefore introduced into France: Grisoutine, a mixture of ammonium nitrate and nitro-glycerine; Blasting Powder P, ammonium nitrate and collodion cotton; and Grisounite, ammonium nitrate and nitro-aromatic compounds such as nitro-naphthalene.

The great drawback to the use of ammonium nitrate is its hygroscopic nature, but the tendency to absorb water from the atmosphere has been overcome to a great extent by coating the grains with paraffin-wax or other waterproofing material, and by enclosing the cartridges in suitable envelopes.

England. In Germany and England it has long been recognized that the temperature of explosion is only one of the factors in making an explosive safe or dangerous to use in fiery mines, and consequently reliance has been placed more upon trials in testing galleries, which are intended to imitate as nearly as possible the conditions in a mine. The North of England Institute of Mining and Mechanical Engineers appointed a Committee in 1888 to inquire into this matter. Their trial gallery at Hebburn Colliery was completed in 1892, and after experimenting with various explosives until 1895 they recommended the use of several, the majority of which were ammonium nitrate explosives.

It was upon the results obtained by this Committee that the Coal Mines Regulation Act of 1906 was founded. This Act, which is still in force, authorizes the Home Secretary to prohibit the use of any explosive in coal-mines, and to appoint Inspectors of Explosives to administer the Act. A testing gallery was erected in Woolwich Arsenal, and there all explosives had to be tested before they were permitted to be used in coal-mines in the United Kingdom. More recently a larger testing gallery has been erected at Rotherham, where tests can be carried out on lines more nearly approaching those that have been adopted in Germany and Belgium.

Cheddite. In 1897 F. A. G. Street took out patents for explosives consisting of potassium chlorate mixed with castor-oil in which aromatic nitro-compounds are dissolved. The great sensitiveness of chlorate mixtures is thus overcome.

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The explosive thus produced is called Cheddite, and is used largely in England, France, and Germany.

Inspection of explosives.

In 1875 was passed the English "Explosives Act," which has had such a great influence upon the development of the explosives industry. Its form was largely due to the late Colonel Sir V. D. Majendie, who was appointed the first permanent Inspector of Explosives to administer its provisions. The necessity for legislation was revealed by an explosion at Messrs. Ludlow's, at Birmingham, which caused the death of fifty-three persons. Colonel Majendie was instructed to report upon it. Previous to this there had been many other accidents large and small, including that of two powder magazines on the banks of the Thames at Erith, which killed thirteen people and did great damage to property.

The Inspectors of Explosives were given power to inspect all magazines and factories and see that operations are carried out in a reasonably safe manner. As a result the number of deaths in explosives factories has been very greatly reduced in spite of the fact that the number of people employed is several times as great :

	Average number killed per annum in explosives factories
1868–1870	43
1871–1874	32
1878–1887	7·5
1888–1897	5·2
1898–1907	6·9
1908–1913	7·0

By the wise and tactful manner in which they carried out their duties Colonel Majendie and his colleagues conferred this great benefit upon the employees in the explosive factories without in any way seriously interfering with the development of the industry. In fact, the precautions, which the inspectors insisted on, have been advantageous to the shareholders as well as to the workpeople and the general public. In 1898 Sir Vivian Majendie died in harness, but the work has been carried on in the same spirit by his successors, Colonel Ford, Captain J. H. Thomson, and Major A. Cooper-Key, and the other Inspectors of Explosives working under them. The provisions of the English Explosives Act of 1875 have been largely adopted in the legislation of foreign countries, British Colonies, and India.

Smokeless powders.

It has already been pointed out that the early attempts of von Lenk and others to make a satisfactory smokeless powder from gun-cotton were unsuccessful because it was much too violent in its effects. The gun-cotton being in a state of fine fibre interspersed with air spaces the explosion travelled through it almost instantaneously. Black powder, on the other hand, being a mechanical mixture, the explosion can only start at the points where the particles of saltpetre are in actual contact with the particles of

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sulphur and charcoal, consequently the time of explosion is comparatively long.

The first successful smokeless powder was that of Major Schultze, of the Prussian Artillery. First, he appears simply to have impregnated little grains of wood with saltpetre,[1] but afterwards he purified the wood to some extent by washing, boiling and bleaching it, and then nitrated it, and purified the nitrated lignose by much the same process as that used by von Lenk for gun-cotton. The grains thus obtained were then impregnated with saltpetre, alone or mixed with barium nitrate.[2] This was introduced about 1865. According to an analysis published by Cundill in the *Dictionary of Explosives*, the nitro-lignin contained more than 20 per cent. of unnitrated lignin. This and the different physical structure of wood as compared with cotton made the material burn more slowly in the gun, and the rate was still further reduced by the addition of the nitrates of potassium and barium. The explosive was still too violent for rifles, however, but was found to be quite suitable for shot-guns. The Austrian rights to Schultze's invention were acquired by a firm called Volkmann's K.K.priv. Collodinfabriks Gesellschaft, H. Pernice and Co. Volkmann took out Austrian patents in 1870 and 1871, which were kept secret at the time, but Guttmann obtained copies of them and published translations in his *Twenty Years Progress in Explosives* (Whittaker, 1909). From these it is seen that Volkmann had made the further step of partly gelatinizing the grains by treating them with a mixture of ether and alcohol, whereby the explosion would be restrained still more. This powder was made under the name of Collodin from 1872 to 1875, but then the Austrian Government stopped the manufacture on the ground that it was an infringement of their gunpowder monopoly. The nitro-lignin made as described by Volkmann must have been decidedly impure and, therefore, unstable, and difficulties were no doubt experienced in obtaining uniform results.

Schultze powder.

1865.

A company was formed in England in 1868 to work Schultze's invention, and a factory was established at Eyeworth, in the New Forest, in 1869, and this after a time achieved great success. By 1881 Schultze powder had become so popular with sportsmen on account of the light recoil and absence of smoke as compared with black powder, that the London gun-makers found irksome the restrictions upon the quantities they were allowed to store. The manufacturers of this powder have modified their methods from time to time to meet the demands of sportsmen and to keep abreast of the general advance in the technology of explosives, so that the Schultze powders are still amongst the best.

The next successful smokeless powder was invented at the works of the Explosives Company at Stowmarket, which formerly belonged to Thos. Prentice and Co. It was protected by patent No. 619, taken out in 1882 by

E. C. powder 1882.

[1] Sanford, *Nitro-Explosives*, 1896, p. 173.

[2] Eng. Pat. 900 of 1864.

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Walter F. Reid and D. Johnson. This was called E. C. Powder (Explosives Company), and consisted of nitro-cotton mixed with the nitrates of potassium and barium with the addition of colouring-matter and small quantities of other organic compounds. It was made into grains which were hardened by being partially gelatinized by means of a solvent, ether-alcohol. A separate company was formed to work the invention, and a factory was started at Green Street Green, near Dartford, in Kent. This is still in existence, and E. C. Powder continues to be much used.

Gelatinized powders.

For use in rifled fire-arms these powders are too quick. For this purpose it has been found necessary to destroy entirely the structure of the original cellulose by thoroughly gelatinizing it. The first to produce a good smokeless rifle powder was the French engineer Vieille, working on behalf of the French Government in 1886. He incorporated the nitro-cotton with ether-alcohol in a machine such as is used for kneading bread. The resulting paste was rolled out into thin sheets and cut into small squares and dried. The powder was called Poudre B, after General Boulanger. In 1888 Nobel invented a powder called Ballistite, consisting of a nitro-cotton of low nitration gelatinized with nitro-glycerine, and in the same year an English committee adopted Cordite, a mixture of highly nitrated gun-cotton, nitro-glycerine and vaseline (mineral jelly), gelatinized by means of acetone.

Every nation now uses propellants consisting principally of gelatinized nitro-cotton either by itself or mixed with nitro-glycerine. These gelatinized powders when suitably ignited in the gun burn from the surface inwards, consequently the time of explosion can be increased by making the individual pieces of explosive bigger. Without altering the composition powders can be produced suitable for every sort of rifled fire-arm from a pistol to a 14-inch gun.

Picric acid.

It has already been mentioned that Sprengel had in 1871 pointed out that picric acid by itself can be detonated. No practical use was made of it until about 1886, when Turpin proposed to use it for filling high explosive shells, the picric acid being compressed and agglomerated with a solution of gum arabic, or oils or fats or collodion jelly.[1] This was adopted by the French Government under the name of Melinite. Other high explosives are mostly too sensitive to use in shell: they are liable to explode in the bore of the gun from the shock of discharge. For this reason gunpowder only was previously used for filling shell, and it still forms the bursting charge of shrapnel shell and other sorts which only require a moderate disruptive power. Picric acid, however, is nearly as insensitive as black powder and can therefore be used with safety for shell. In fact, it requires a very powerful detonating primer to ensure complete detonation. With various modifications picric acid has been adopted in almost every country for this

[1] *See* Eng. Pat. No. 15,089 of 1885.

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purpose. It has the disadvantage, however, that it readily forms picrates if it comes in contact with metals or earthy materials, and these picrates are much more sensitive than picric acid. There is a tendency now to use trinitro-toluene instead. This substance has the further advantage of a much lower melting-point, which makes it much easier to pour the molten substance into the shell.

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PART II

BLACK POWDER

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CHAPTER IV

MANUFACTURE OF SALTPETRE

Nitre deposits : French saltpetre industry : Artificial nitre beds : English saltpetre industry : Formation of nitrates : Berthelot's researches : Bacterial action : Indian saltpetre industry : Indian refinery : Chili nitrate deposits : "Conversion" saltpetre : Refining saltpetre : Saltpetre from the atmosphere

So far as is possible in the almost entire absence of all records, an account has been given in Chapter I of the first discovery of saltpetre.

Nitre deposits.

Until the middle of the nineteenth century all saltpetre was obtained by dissolving it from earth and deposits in cellars and caves and similar places, where it had formed naturally. In Europe there are very few localities where nitrate can accumulate in the soil to such an extent that a profit could be made by extracting it. There is no prolonged dry season during which deposits can form without being washed away again. Consequently saltpetre could only accumulate in sheltered places, such as cellars and stables, especially those in which there was much nitrogenous matter undergoing decomposition. As it was of the utmost importance in every country to have a sufficient supply of saltpetre, especially in time of war, its production formed the subject of royal decrees and orders at an early date. In France, officers (salpêtriers commissionés) were appointed in 1540 to search for and extract saltpetre, and no doubt the industry was in existence some time before.[1] This edict was confirmed and renewed in 1572, and again whenever France was waging a serious war. The saltpetre workers operated on the earth of stables, sheep-pens, cattle-sheds, cellars and pigeon-houses, and on the plaster and rubbish removed when houses were pulled down. They had the right to gather material everywhere, with scrapers and brushes in the houses, with picks and shovels in places not inhabited. No building or wall could be pulled down until notice had been given to the saltpetre workers, who stated which parts they wanted reserved.

French saltpetre industry.

In the eighteenth century, the saltpetre workers in France received many additional privileges. For instance, they could set up their vats and other plant in public halls, private courtyards or wherever they thought fit. The local authorities had to supply the wood required for heating, and provide

[1] Berthelot, *Sur la Force des Matières explosives*, 1883, vol. i., p. 345 *et seq.*

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carts for transporting the plant and the saltpetre to the refinery. As a rule each locality was visited once every three years.

Artificial nitre beds.

Saltpetre was also obtained from artificial nitre-beds, consisting of earth mixed with animal and vegetable matters, ashes, refuse of buildings, lime and marl. This was all placed in a large barn, and collected in heaps mixed with twigs and intersected with holes to allow access of the air. It was turned over also from time to time and watered with urine. Nitrate gradually formed in the mass and was extracted with water. There were many modifications of this process adopted in different places.

In the reign of Louis XIII (1610 to 1643) the annual crop of saltpetre amounted to 3,500,000 lb., but it gradually diminished in the eighteenth century largely on account of the strong objection the people naturally had to the presence of saltpetre workers in their houses and domains. In 1775 the quantity had fallen to 1,800,000 lb., and half the annual requirement was imported from India. If it had not been for the many privileges the nitrate workers enjoyed, the home product could not have competed at all with that imported from India. In 1789, the year of the fall of the Bastille, a great effort was made, however, to revive the industry, and 3,000,000 lb. were obtained. In 1791, however, the National Assembly proposed to abolish the privileges of the saltpetre workers, but war broke out, the harbours of France were blockaded, and it became necessary to produce in the country all the saltpetre for the powder required. The recent increase of chemical knowledge and the hearty co-operation of the greater part of the population made it possible to produce 16,000,000 lb. in a single year, and 5,000,000 in the next. The whole organization was placed under the control of the department of " Poudres et salpêtres," which still continues to regulate matters concerning explosives.

When peace was finally re-established, the renewed competition of Indian saltpetre dealt a severe blow to the industry in France, and in 1840 the bounties were abolished, but it struggled on until the exploitation of the sodium nitrate deposits in Chile and the potash deposits in Germany in the second half of the nineteenth century led to the production of artificial saltpetre. The consequent reduction of price almost entirely killed the French saltpetre industry, and in 1870, when a scientific committee was engaged in providing Paris with all stores necessary for its defence, Berthelot could find only one or two small producers in Champagne.

English saltpetre industry.

In mediæval England saltpetre was obtained by the same methods as in France and other countries, that is by extracting the earth from stables, dovecots etc., and the creation of saltpetre " plantations." In 1558, Queen Elizabeth granted a monopoly for gathering and working saltpetre for eleven years to George Evelyn, Richard Hills and John Evelyn.[1] The monopoly

[1] George Evelyn, who is said to have learnt the industry in Flanders, was the grandfather of John Evelyn the diarist. (*Rise and Progress of English Explosives Industry*, p. 18.)

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included the whole of the south of England and the Midlands, except the City of London and two miles outside it.

The Evelyns seem to have been the first to make gunpowder on a large scale in England. In 1596 they bought up also the saltpetre monopoly for London and Westminster.

In 1626 the East India Company, then in its infancy, was importing saltpetre into England. It erected powder mills in Surrey, and when its Charter was renewed in 1693, it was stipulated that 500 tons of saltpetre should be supplied every year to the Ordnance. Ever since then, Indian saltpetre has been used very largely in England for the manufacture of gunpowder.

Formation of nitrates.

Whence come these large quantities of nitrates? The nitrogen of the atmosphere does not form chemical compounds at all readily. Under the influence of lightning, and high tension electricity generally, small quantities of nitric acid are formed and these are carried down by rain into the soil and rendered available for plant life. But Lawes and Gilbert in their researches at Rothamsted found that the amount of nitrogen removed with the crops was more than the total sum of that added as manure, and brought down by the rain together with the loss of nitrogen from the soil. No plants can grow without absorbing nitrogen compounds from the soil; and when animal and vegetable matters decompose, a portion of the combined nitrogen is liberated as nitrogen gas, but in spite of this steady loss there is no indication that the surface of the earth as a whole is becoming poorer in combined nitrogen.

Berthelot's researches.

Berthelot investigated this matter about 1876 and discovered that nitrogen and oxygen also combined under the influence of electricity of quite low tension, such as that yielded by two or three electric cells, although only very slowly, and moreover that in the presence of carbohydrates such as dextrine the combination was considerably more rapid.[1] Although the quantities thus obtained in small laboratory experiments only amounted to a few milligrammes in several months, yet, as there are always differences of potential of this order over the whole surface of the globe between the earth and the air above it, he considered that this phenomenon was sufficient to account for all the nitrates and other compounds of nitrogen that are formed.

Bacterial action.

Since then, however, it has been found that this is by no means the only cause of the formation of nitrogen compounds from the nitrogen of the atmosphere. There are bacteria in the soil, which can take up nitrogen from the air and cause it to combine with other elements to form nitrates and more complex bodies such as albuminoids. Some of these, such as Azobacterium Chroococcum Beijerinck, can live and act freely in the soil; others seem only to exist in the nodules that are found on the roots of certain sorts of plants. The Bacterium Radicicola is perhaps the most important of these; it is found on the roots of the leguminosæ (beans, peas), and renders it possible for these

[1] *Sur la Force des Matières Explosives*, 1883, vol. i., chap. vi.

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crops to grow on otherwise sterile soil, which afterwards is able to support other crops. Some other plants such as the alder tree have similar nodules on their roots. There are some soil bacteria also, which convert nitrates into nitrites, others carry out the reverse change, others again liberate nitrogen from nitrates or nitrites, and several of these actions may be going on simultaneously in the soil.

Bacterial action proceeds most rapidly in a warm moist climate like that of Bengal. The accumulation of nitrate to such an extent, that it can readily be collected in large quantities, also requires that there shall be regular seasons of the year when little or no rain falls. In this respect, Bengal and most other parts of India satisfy the conditions.

Indian saltpetre industry.

Bihar is the principal seat of the saltpetre industry in India, but considerable quantities also come from the United Provinces and the Punjab, and smaller amounts from other parts of India and from Burma. Except what is consumed in the country, the greater part is exported from Calcutta. Fifty or sixty years ago, the average quantity exported was over 30,000 tons per annum, now it is 18,000 to 20,000. In the places where the nitrous earth is collected the natural vegetation is scant, as the soil in many cases is too salt for crops to grow even during the rains. It is obtained in and around existing village sites and on the mud walls of houses and cow-sheds. In the rainy season, lasting from June to October, the process of nitrification goes on in the warm moist soil, assisted by the addition of nitrogenous refuse. The following account by R. W. Bingham,[1] gives a clear picture of the industry in the last century :

" It is all made by a peculiar caste called ' nuniah,' and, so far as my experience shows, is principally in the hands of . . . ' mahajuns,' who make yearly advances, charging 12 per cent. for the same. The ' nuniahs ' are a tolerably safe class, compared with the ordinary ' riot ' (peasant), to deal with, and pay the ' zemindars ' (landowners) a comparatively large price (if measured by the ' bigah ') for the old walls and old sites in which they revel. The supply of saltpetre from these old sites appears to be practically inexhaustible ; for we find the ' nuniah ' very busy making up his piles just after the setting in of the rains. This earth he exposes to the sun and rain, and takes care, by erecting walls, etc., that the precious stuff is not wasted away. A casual visitor would not be able to understand what he is after, but when the hot suns of April, May and June come on, then himself and his family boil merrily away, and eliminate saltpetre and salt from this apparently useless soil. Then the ' mahajan ' is on the look-out and secures the saltpetre as it is made, and carries it to his own refinery for final manipulation ; while the salt which is always bitter, and I should say unwholesome, under the name of

[1] *Jour. Agricultural and Horticultural Soc.*, xii., p. 107, old series ; *Dict. Economic Products of India*, S. 686, vol. vi. part ii. p. 437

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'khari nimuk' is sold to the lowest classes of the community at a cheap rate. The business must be a profitable one, as the large bankers of Ghazipore, Patna and Benares are always ready to go into the trade, and to advance money to responsible middlemen. . . . Sometimes these men experience considerable trouble in recovering their advances, but in that case they quietly walk off with the bullocks of the 'nuniah' who . . . never dreams of making a complaint, but

FIG. 1. Percolators for Extracting Indian Crude Saltpetre

begs or borrows from his comrades and friends till he has got money enough to release them by paying back principal and interest; well knowing that he will get no more advances, and will, besides, be put out of caste by his caste-mates if he does not, at all events, pay the original advance. If, on the contrary, he makes more saltpetre than will cover his advance, and he has no particular ceremony going on, he will clandestinely sell his partially refined saltpetre to other petty purchasers, and get drunk while the money lasts, and ask contemptuously, 'What, am I a poor man that I should work?'

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The trade is too hazardous a one, and the petty advances spread over too wide an extent of country to make it worth the while of Europeans with capital to attend to; in consequence it is almost wholly in the hands of the large houses above named (who are connected with Calcutta native firms, and who in turn have their small branches in every petty town in the district)."

The industry is conducted on the same lines now as then, except that it

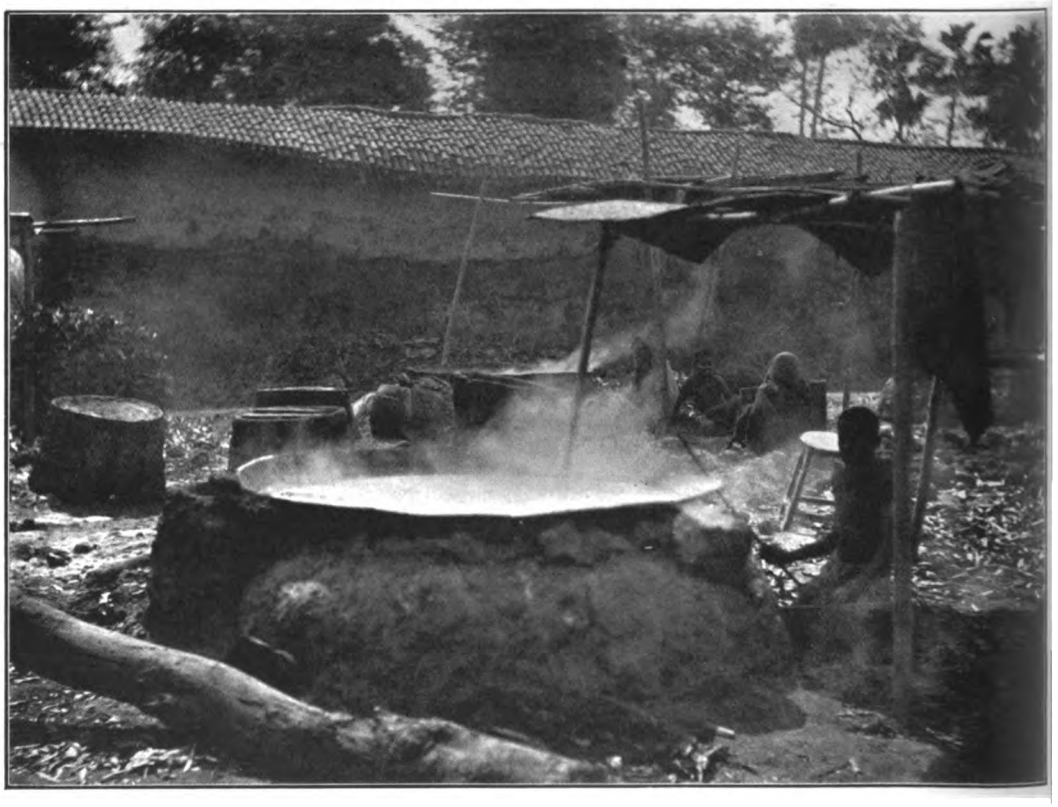

FIG. 2. Evaporating Liquor from Percolator

is not as remunerative as it used to be. Hooper [1] made analyses of a large number of samples of the earth collected by the "nuniahs": the amount of nitrates in them varied from 1 to 27 per cent., but as a general rule they contain 3 to 5 per cent., also several per cent. of sodium chloride and sulphate. A description of the process of extraction has been given by Leather and Mukerji [2]

The "nuniah" builds an earthen chamber called the "kuria" or "kothi"

[1] *Agricultural Ledger*, 1905, No. 3.

[2] *Bulletin* No. 24 of the Agricultural Research Institute, Pusa, 1911; *S.S.* 1912, 116 and 136.

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with wet mud, which is allowed to dry. This chamber (*see* Fig. 1) has either circular walls some 5 or 6 feet in diameter, or oblong walls, and a floor which slopes slightly from back to front. In the front wall is a hole at the level of the bed, which allows the nitrate liquor to drain away into a pot. Above the bottom of this earthen chamber a false bottom is laid, consisting of bamboos and matting placed on a few loose bricks. The nitrate earth is filled in on this with great care. Stones, etc. are removed from it as far as possible, and it is put in slightly moist and trodden down so as to leave no channels, through which the water would run too rapidly. Wood ashes are generally mixed with the earth, so that the potash in them may convert into saltpetre the nitrates of lime and magnesia. A small piece of matting is placed over the top of the earth and water is poured on cautiously. The liquor that percolates through first is fairly strong : it is transferred to shallow earthenware or iron basins and evaporated down (Fig. 2) by means of a fire of wood, leaves or twigs, or in the Punjab to shallow masonry trays in which the concentration takes place through the action of the very dry air and the heat of the sun. The weak liquor that percolates through afterwards, is thrown on to a heap of already extracted earth, where it evaporates : this earth is afterwards extracted again. The strong liquor is boiled down until crystals begin to appear, and then is allowed to cool ; the crystals are then fished out, fresh liquor is added to the mother liquor and the concentration is carried out as before. The composition of the crude saltpetre thus produced varies considerably. Hooper gives the analysis of fifty-five samples and of these the following have been selected by Leather as being typical:

	Farukhabad		Okara		Mozaffarpore	Burhanpura
	I	III	I	III		
Potassium nitrate	66·07	44·92	53·00	26·86	49·36	68·40
Calcium nitrate	—	—	2·60	—	3·28	2·60
Magnesium nitrate	2·54	4·80	—	12·24	7·44	2·12
Sodium chloride	21·84	35·38	34·22	34·80	16·82	17·98
Sodium sulphate	3·65	10·00	3·88	11·20	14·60	3·40
Insoluble matter	·90	1·20	1·10	1·40	1·50	1·70
Water	5·00	3·70	5·20	13·50	7·00	3·80
	100	100	100	100	100	100

No attempt is made to separate the sodium chloride at this stage because there is an excise duty on it, and the salt department only allows the recovery to take place in the refineries, where a proper control can be kept. Some

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of the crude saltpetre is used as manure, but the greater part goes to the refinery.

Indian refinery.

In the refinery the processes are very similar to those carried out by the "nuniah." There is always a large heap of saltpetre earth, which is worked over and over again, the weak liquors being always thrown on to it. This is extracted in "kothias," but the strong liquors are not evaporated down by themselves; crude saltpetre is dissolved in them at the boiling-point. The quantity added is such that the potassium nitrate is all dissolved to form a boiling saturated solution, whereas the greater part of the sodium chloride remains undissolved (see Table of Solubilities on p. 52) together with the insoluble matter. The hot liquid is allowed to settle for a little while, and then run into wooden vats where it is allowed to cool slowly and deposit crystals of potassium nitrate. The residue in the dissolving tank is washed with water to recover the saltpetre in it, and the common salt may be purified by dissolving it in weak nitre liquor, decanting off and evaporating down. The insoluble matter and all weak liquors are added to the heap of earth, which steadily grows from year to year. The mother liquor from the crystallization of the saltpetre is also added to it after it has been used three or four times, as it is then too impure.

The refined saltpetre is in large crystals of a brownish colour. To purify it further and improve the colour it is sometimes subjected to a washing process: it is put in sacks over wooden tubs and cold water is poured through it. This of course dissolves some of the potassium nitrate as well as the impurities, and is consequently returned to the refinery process. Leather and Mukerji give the following analyses of refined saltpetre before and after washing:

	Burhanpura		Savan		Bakramau	
	Unwashed	Washed	Unwashed	Washed	Unwashed	Washed
Potassium nitrate	90·70	94·91	81·98	91·55	88·63	94·70
Potassium sulphate	—	—	5·44	·93	·15	·15
Sodium sulphate	·91	·03	—	—	—	—
Potassium chloride	—	—	2·59	2·51	6·06	2·67
Sodium chloride	5·40	3·12	7·05	1·68	·07	·10
Sand	·30	·20	·20	·35	—	—

Leather has designed a simple plant on more up-to-date lines to carry out the refining process, and is endeavouring to get the Indian refiners to take it up. This consists of a dissolving vessel provided with a stirrer, a filter in which the liquor is rapidly filtered at a high temperature, and a series of coolers in which the saltpetre is caused to crystallize rapidly. The crystals

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are then freed as far as possible from the mother liquor in a centrifugal machine. The saltpetre produced has a purity of 90 to 93 per cent.

Chili nitrate deposits.

The plain of Tamarugal in Chili is even more favourably situated than Bihar or Bengal. It lies between the Andes and the comparatively low Coast Hills at a height of about 3000 feet above the sea within the tropics. As a rule there is very little rain there, but about once in six or seven years the plain, which is about 45 miles wide, is flooded. The plain slopes gently towards the Coast Hills and as there is no outlet for the water, it collects there and evaporates, and all the nitrate it has dissolved from the entire plain is deposited in a comparatively narrow area. The entire product of the bacterial action upon many hundreds of square miles for many centuries is found in the Chili nitrate beds. As the soil contains sodium compounds and very little potassium, it is sodium nitrate that has been deposited.[1]

During the Crimean War (1854–1855), the demand for saltpetre was so great that the existing sources of supply in Europe and India did not suffice, and considerable quantities were made from Chili nitrate, which had been supplied to Europe in constantly increasing quantities since 1830. The salt beds at Stassfurt, however, did not commence to yield potassium chloride (Carnallite) until about 1863, therefore other sources of potash had to be used to convert the sodium nitrate from Chili into the corresponding potassium salt. The only sources of potash then available were kelp, and the ash of wood, etc. When the war was over, saltpetre prepared in this way could no longer compete with the natural product from India. But shortly afterwards fresh sources of potash were found in " suint," the dried sweat of sheep, which is washed from the wool, and in the cinder of " vinasse " (Schlempekohle), which is obtained as a by-product in the refining of beet sugar. With the development of the Stassfurt potash industry these lost their importance however.

"Conversion" saltpetre.

Large quantities of potassium nitrate are now made by the interaction of Chili nitrate and commercial chloride of potash, which is made by lixiviating "carnallite," a double chloride of potassium and magnesium, occurring in immense deposits near Stassfurt in Germany. In the heated and concentrated mother liquor from a previous operation commercial sodium nitrate (about 95 per cent. purity) and potassium chloride (not less than 80 per cent. purity) are dissolved, the nitrate being in slight excess. Of the four salts that might be present in the solution thus formed, sodium chloride has the least solubility at a high temperature and potassium nitrate the greatest (*see* Table on p. 52). At a low temperature potassium nitrate has the lowest solubility. The figures are of course for pure salts dissolved in distilled water, and the presence of other substances in solution would alter the solubilities somewhat, but the figures given in the last two columns, the solubilities of sodium chloride and

[1] *See* Newton, *J.S.C.I.*, 1900, p. 408.

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potassium nitrate in water which is simultaneously saturated with both salts, show that in this case the salts have little effect upon one another's solubility. Consequently in the hot concentrated solution of sodium nitrate and potassium chloride most of the sodium chloride is precipitated out :

$$NaNO_3 + KCl = KNO_3 + NaCl$$

TABLE OF SOLUBILITIES

Temperature	Gramme mols. per 1000 g. water					
	One salt only present				When water is saturated with KNO_3 and NaCl	
	NaCl	KCl	$NaNO_3$	KNO_3	KNO_3	NaCl
0° C. . . .	6·10	3·70	8·54	1·31	1.8	5·6
20 . . .	6·14	4·56	10·3	3.12	3.4	6·5
40 . . .	6·24	5·36	12·2	6·32	6·0	6·4
60 . . .	6·36	6·11	14·5	10·9	9·9	6·0
80 . . .	6·53	6·85	17·4	16·7	16·5	6·2
100 . . .	6·75	7·60	20·9	24·3	28·0	6·9
120 . . .	6·84	8·43	25·1	38·9	38·0	7·2

Calculated from figures in Seidell's *Solubilities of Inorganic and Organic Substances*, 1907. A "gramme-mol" is the molecular weight of a substance in grammes. To find the actual weight of the salts dissolved by 1000 parts of water, multiply the above figures by the corresponding molecular weights : for NaCl 58·5, KCl 74·6, $NaNO_3$ 85·1, KNO_3 101·1.

The solubilities of these different salts in the presence of one another have recently been investigated by J. W. Leather and J. N. Mukerji, whose results do not differ very greatly from the above. At temperatures below 30° C., however, they found that a small proportion of KCl is formed in a solution saturated with KNO_3 and NaCl, and a corresponding amount of solid $NaNo_3$ is deposited. At temperatures above 30° C. on the other hand KCl is deposited and $NaNO_3$ formed in solution, and as the temperature rises the quantities of these salts increase rapidly.

The liquid is boiled for half an hour to complete the reaction as far as possible, then it is run through a filter into shallow cooling tanks ; some more water may now be added with advantage to prevent sodium chloride separating out with the potassium nitrate.

The solution is kept stirred whilst it cools, so that the potassium nitrate may separate in small crystals, which do not contain so much mother liquor as large ones. The crystals are drained and then washed with the liquors from the next crystallization. This is best done in a centrifugal machine, as the quantity of washing liquor is thereby reduced to a minimum.

The crude saltpetre thus obtained still contains several per cent. of sodium

[1] *Mem. of Dept. of Agriculture of India*, Chemical Series, vol. iii., No. 7, 1914.

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chloride and about half a per cent. of magnesium chloride. It is purified by dissolving in the washings of the purified salt, allowing it to crystallize, and washing with water, whereby the percentage of chloride is reduced to 0·05 per cent. or less and the material is rendered practically free from all other impurities. Finally it is dried.

The sodium chloride formed in the conversion is washed on the filter with liquors containing gradually diminishing amounts of nitrate, until the solid contains only 0·8 per cent or less. This " saltpetre salt " then contains about 98 per cent. of sodium chloride in the dry state. It is unsuitable for the manufacture of hydrochloric acid, because this would be contaminated with nitrous compounds, and moreover the plant would be strongly attacked.

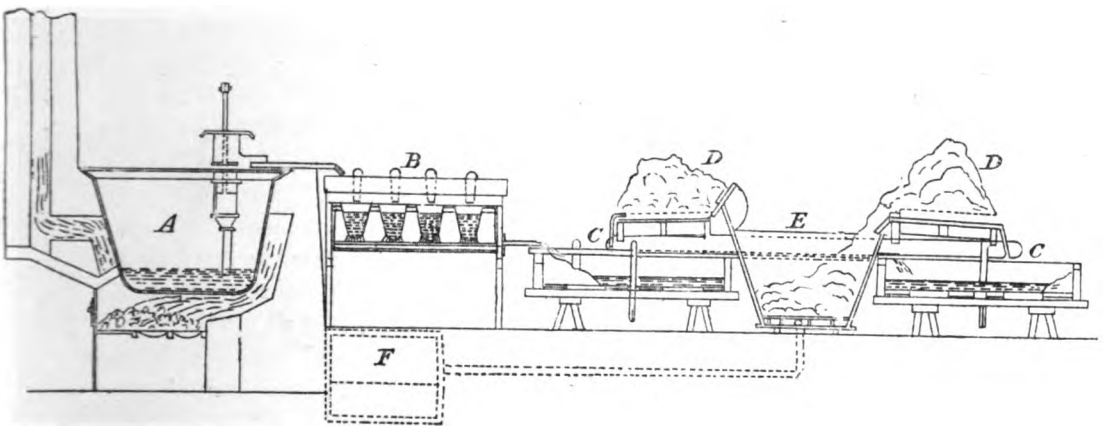

FIG. 3. Plant for Refining Saltpetre at Waltham Abbey

It is therefore either sold to farmers to put on the land or used in copper extraction or other metallurgical processes.

" Artificial " or " conversion " saltpetre made as above, is usually supplied by the chemical works to the explosives factory in such a state of purity that no further purification is necessary. Natural saltpetre from India on the other hand always contains a considerable amount of impurity and requires to be refined before use.

Although the quantity of black powder made is still very considerable, it is not nearly so large as it was twenty years ago. The black powder factories now being worked were all in existence at that time, and they mostly have large saltpetre refineries attached, which more than suffice to refine all the material that they require. It has not been found worth while to reconstruct the refineries, as they are still capable of turning out saltpetre of good quality. It would nowadays be possible, however, to erect up-to-date plant that would save much space and some fuel and labour.

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Refining Indian saltpetre. At Waltham Abbey, as at some other English powder factories, Indian saltpetre is used exclusively. The total quantity imported into England every year is, however only 10,000 tons and the total consumption for making powder, etc., several times that amount. The balance is made up with "conversion" saltpetre.

Waltham Abbey method. The method of refining still followed at Waltham Abbey is as follows: The crude or "grough" saltpetre is dissolved up in a large iron copper, *A* (Fig. 3), which has a capacity of 500 gallons, and is fitted with a perforated false bottom which prevents the saltpetre adhering to the vessel. For each charge, about 25 cwts. of grough saltpetre are taken, and 5 cwts. of crystals recovered from liquors, and 5 cwts. of crystals left in the crystallizing cisterns. This is all dissolved in about 280 gallons of the washings of the purified saltpetre, which also contains a considerable amount of the salt. The fire is lit under the copper, and in about two hours the saltpetre is dissolved and the liquid boiling. Just before it boils a thick scum rises to the surface consisting mostly of impurities. This is skimmed off and the false bottom is removed, and cold water is added from time to time to induce fresh scum to form, if it will. The fire is then withdrawn and the liquid is allowed to settle for two hours. Then a hand pump is lowered into the copper and the liquid is pumped into filters *B*, where it passes through linen cloth. From here it runs to shallow copper crystallizing troughs *C*. As it cools down, the liquid is kept stirred by a workman in order to make the saltpetre separate in small crystals, and the saltpetre "flour" as it forms is drawn up on to an inclined draining platform *D*, and from there is passed to a washing vat *E*. After the temperature has fallen to about 32° *C*. (90°F.) the solution is no longer stirred and any crystals that form after that are treated as grough nitre.

Washing. The washing vat *E* is about 6 feet long, by 4 feet wide, by 3 feet 6 inches deep, and is fitted with a false bottom made of wood with small holes bored in it. Below the false bottom is a plug which can be removed to allow the washings to flow away. First the charge is washed with 70 gallons of water sprinkled over it by means of a rose, the plug being left out so that the washings can drain away to a liquor tank *F*. After draining half an hour the plug is inserted and the saltpetre covered with fresh water, which after standing half an hour is also allowed to drain into *F*. Finally the salt is washed by sprinkling with 100 gallons of water, the plug remaining out. The saltpetre is now allowed to drain all night and is then removed to the store house where it is allowed to dry spontaneously. In about three days the moisture has fallen to 3 or 5 per cent.

Mother liquor. The mother liquors and other impure solutions are boiled down to about a quarter of their original volume. Any scum or deposit that forms during the boiling should be removed and water then be added. The solution is now

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filtered and allowed to crystallize. The crystals are treated as grough saltpetre and the mother liquor returned to the evaporating pots.

Continental methods.

The methods of refining adopted in France, Germany and other countries are substantially the same as that at Waltham Abbey. A small proportion of size is, however, often added in the refining copper to assist the formation of scum.

Saltpetre from the atmosphere.

Potassium nitrate could also be made from the calcium nitrate produced from atmospheric oxygen and nitrogen by processes, such as that of Birkeland and Eyde as carried out at Notodden, but the calcium chloride obtained as a by-product would be of no value. Or the dilute nitric acid obtained in the Birkeland-Eyde process could be treated with limestone or chalk and potassium chloride :

$$CaCO_3 + 2KCl + 2HNO_3 = 2KNO_3 + CaCl_2 + CO_2 + H_2O$$

In this case the carbonic acid could be collected and compressed into cylinders and sold. Up to the present, these methods do not appear to have been adopted,[1] but ammonium nitrate is being made, by neutralizing ammonia liquor imported from England.

[1] Jurisch, *Salpeter und sein Ersatz*, 1908.

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CHAPTER V

MANUFACTURE OF CHARCOAL AND SULPHUR

Charcoal : Wood used : Distillation : Composition : Brown charcoal : Sulphur : Sicilian sulphur : Louisiana sulphur

Wood used. At one time the charcoal for black powder was made almost exclusively from alder-wood, but later other soft woods were used, and straw charcoal was also introduced for the brown powders for heavy ordnance. In England dog-wood is much used, especially for rapid burning powders of small grain ; for larger powders, alder and willow. In Germany alder and willow are the principal woods used ; in Austria, alder and hazel ; in Switzerland, hazel ; in France, alder, poplar, and lime ; in Spain, the oleander, yew, willow, hemp stems, and vine ; in Italy, almost exclusively hemp stems.

Charcoal burnt in heaps or kilns has not been used very largely for gunpowder since even the very earliest days, for it was soon found that to produce good powder it was necessary to select the wood carefully and burn it very uniformly. It has therefore been heated in ovens or iron vessels, and the procedure of the present day does not differ materially from that of the fourteenth century.

The wood should be cut in the spring, as the sap in it at that time of the year contains much less inorganic matter, so that although the proportion of sap is larger, yet the percentage of ash in the wood is much smaller. Moreover, wood cut in the spring is much more easily freed from its bark, which also contains a large proportion of ash. The wood is kept at least eighteen months, and generally not less than three years, to allow the sap to dry out of it and other changes to take place. The practice varies considerably as regards protecting the wood from rain : at Dresden it is kept in sheds ; at Spandau in the open ; at Waltham Abbey also the wood is kept in the open, but the dog-wood is covered with thatch, whereas the alder and willow are not.

The wood is split if necessary into pieces about 1 inch thick, and these are placed in an iron cylinder about 2 feet in diameter and 3 feet 6 inches long. This cylinder is then raised by means of suitable tackle and placed in a furnace, which is heated as uniformly as possible. The higher the temperature and the longer the heating, the lower is the percentage of hydrogen

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and oxygen in the charcoal and the greater is its hardness and the difficulty with which it is ignited. At Waltham Abbey dog-wood for R.F.G. or M.G.[1] powders is heated 4 hours, for R.F.G.[2] 8 hours. Alder and willow for R.L.G.[2] are heated 3½ hours, for R.L.G.[4], P., and Prism[1] Black 4 hours, for P[2] 6 hours.

Distillation.

When the temperature of the wood attains about 280° C. volatile products of decomposition of the wood come off plentifully. These could be condensed by means of a suitable condenser, and worked up into acetate of lime and wood spirit. The charcoal plant of a powder mill is, however, on such a small scale as compared with the factories in which charcoal is produced for metallurgical processes with recovery of the by-products, that it is not usually considered worth while to do this. The volatile products are therefore simply led into the furnace by which the wood is being heated, and so some expenditure of fuel is saved. To enable the gases and volatile products to escape the cylinder has some holes bored in it at one end, and the furnace is provided with a pipe to lead away these products. When the carbonization has proceeded far enough, the flame of the burning gas becomes blue. The furnace is then opened, the cylinder taken out by means of the tackle, and a fresh cylinder of wood put in before the furnace has had time to cool. The cylinder that has been taken out is placed inside a larger cylinder, which has a closely fitting lid, and is there allowed to cool. It is necessary that the cooling should take place out of contact of the air, as otherwise the charcoal will catch fire. Even when cold it at first absorbs large quantities of oxygen from the air, and in so doing may become sufficiently hot to catch fire. Therefore oxygen must only be allowed gradual access to the charcoal: it should not be ground until a week after it has been burnt. Before use it is carefully picked over by hand to remove any that has not been properly burnt, as also any foreign matters that have got into it. Charcoal intended for powders for ordnance should be jet black in colour; its fracture should show a clear velvet-like surface; it should be light and sonorous when dropped on a hard surface, and so soft that it will not scratch polished copper.[1] The yield of such charcoal is 28 to 30 per cent. of the dried wood. For small-arms a more slackly burnt charcoal can be used, and the yield may be as much as 40 per cent. Such charcoal has a reddish-brown colour, which is perceptible in the powder until it has been glazed with graphite.

Composition.

The composition of some typical charcoals is shown in the Table[2] on the next page. Spanish hemp charcoal is usually burnt in pits holding ½ to 1 ton. When the carbonization has proceeded far enough the pit is covered

[1] *Treatise on Service Explosives*, 1907, p. 10.

[2] Noble and Abel, *Trans. Roy. Soc.*, 1875 and 1879; Noble, *Artillery and Explosives*, 1906, pp. 127, 129. "B. & S." means analysis by Bunsen and Schischkoff, "K" by Karolyi, "F" by Fedeow.

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with a woollen cloth on which earth is placed. This probably accounts for the high percentage of ash in the analysis below.

Description	Carbon	Hydrogen	Oxygen	Ash
From P. Powder, Waltham Abbey	85·26	2·98	10·16	1·60
From R.L.G., Waltham Abbey	80·32	3·08	14·75	1·85
From R.F.G., Waltham Abbey	75·72	3·70	18·84	1·74
From F.G., Waltham Abbey	77·88	3·37	17·60	1·15
Curtis's and Harvey, Sporting	77·36	3·77	16·62	2·25
Curtis's and Harvey, Mining	83·74	3·07	10·45	2·74
Spanish, Hemp Charcoal	76·29	3·31	14·87	5·53
German Sporting Powder. (B. & S.)	68·8	3·7	27·5	Trace
Austrian Cannon Powder. (K.)	81·3	2·8	13·6	2·3
Austrian Small Arm Powder. (K.)	82·6	2·9	12·5	2·0
Russian Powder. (F)	72·5	2·9	22·3	2·3

Brown charcoal.

The charcoal for brown or "cocoa" powder was made from rye-straw, which was only carbonized very slightly.[1] It was heated only about half an hour, then taken out of the furnace. The carbonization proceeded spontaneously a little further and then the charcoal cooled. The result was a soft charcoal containing a large percentage of oxygen and hydrogen. In the operation of pressing the powder this became a coherent colloid which bound the other constituents together to a dense impervious mass, which burnt comparatively slowly. The cocoa powder gave the best ballistics in heavy ordnance of any "black" powder ever produced, but it has now been entirely displaced by smokeless powders.

For cheap blasting powder and powder for scaring birds and supplying natives of Africa, etc., charcoal of an inferior quality can be used.

SULPHUR

Sicilian sulphur.

Sulphur occurs native in many volcanic districts, especially in Sicily, and until recent times practically the whole of the world's supply came from there. The sulphur in Sicily is mixed with limestone, the ores containing usually from 20 to 40 per cent. of sulphur. The sulphur is generally extracted from this by a somewhat primitive melting process. The ore is placed in a large kiln, covered over except for some small openings, and the ore is set alight. Part of the sulphur burns away, but in so doing it produces enough heat to melt the rest of it, which is run off into moulds and sold as grough sulphur. The disadvantages of this process are that only about 60 per cent.

[1] Guttmann, *Manufacture*, vol. i., p. 90; Cundill and Thompson, p. 21; *Treatise on Service Explosives*, 1900, p. 110.

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of the sulphur is obtained from the ore, most of the remainder being burnt to sulphur-dioxide, which escapes over the country-side destroying the vegetation. Attempts have been made to introduce more efficient methods whereby practically the whole of the sulphur could be recovered by melting it out with hot brine or steam, or distilling it with superheated steam. These methods have not attained any great success, however, the obstacles being the absence of any local supply of fuel and the backward state of the country. The sulphur is refined by distillation, the principal distilleries being situated in Marseilles Some powder mills have small sulphur refineries of their own, as at Waltham Abbey for instance.

Two sorts of sulphur can be obtained by distillation: flowers and stick sulphur. The former consists of minute crystals, which have been deposited on the interior surface of a large chamber or "dome" into which the vapours have been passed. The flowers contain a small percentage of sulphuric acid formed by the action of the air on the sulphur, and consequently are not suitable for the manufacture of explosives. Stick sulphur, on the other hand, is very pure and only requires to be ground.

For the manufacture of sulphuric acid elementary sulphur is but little used now, as it pays better to roast various ores in which it is combined with metals, such as copper pyrites and zinc-blende, but it does not pay to extract sulphur as such from these ores. A certain proportion of it comes on the market however, as it is obtained as a by-product in the Leblanc soda process. The sulphuric acid used in that process is ultimately converted into calcium sulphide, CaS, and for many years this accumulated in great heaps, which were a public nuisance, no method being known by which it could be worked up except at a prohibitive cost. Eventually the Claus-Chance process was devised and perfected, which enabled this to be done. Kiln gas is passed over the "soda-waste," converting it into calcium carbonate and sulphuretted hydrogen: $CaS + H_2O + CO_2 = CaCO_3 + H_2S$. As the sulphuretted hydrogen is rather dilute and variable in concentration, the gas is led through a fresh quantity of the waste, by which it is absorbed forming the bisulphide: $CaS + H_2S = CaH_2S_2$. When kiln gas is led through this the sulphuretted hydrogen is again given off, but is of double the previous concentration: $CaH_2S_2 + H_2O + CO_2 = CaCO_3 + 2H_2S$. This gas is collected in a gas-holder, and can be fed from there into the chambers where it is converted into sulphuric acid, or it can be mixed with gas from the pyrites burners, whereby sulphur is caused to deposit in accordance with the equation: $2H_2S + SO_2 = 2H_2O + 3S$. The sulphur thus obtained is of considerable purity.

Sulphur is also obtained in the purification of coal-gas from sulphuretted hydrogen and other sulphur compounds.

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Louisiana sulphur.

Until recently the market was entirely controlled by an English association, the Anglo-Sicilian Sulphur Company, formed in 1895. Sulphur had been found in Louisiana in 1865, during some boring operations for petroleum, but it was situated underneath 500 feet of quicksand, and all attempts to work it commercially failed until the matter was taken up by Hermann Frasch in 1891, and even then years of work were required and a large amount of capital before success was achieved. The sulphur is mixed with a much smaller proportion of limestone than in Sicily, the ore containing about 70 per cent. sulphur. The method that has been adopted is to put down a pipe of 10 inches diameter until the sulphur deposit is reached, then the hole is continued with a 9-inch drill through the sulphur deposit, which is about 200 feet thick. A 6-inch pipe is passed to the bottom, and a 3-inch pipe through this, both being perforated near their lower ends. Superheated water is passed down the 6-inch pipe, and the sulphur passes up the 3-inch. At first it was raised by means of pumps, but now air is forced down: this mixes with the sulphur and reduces its density, and it is raised to the surface of the ground by the pressure of the water used for melting.

The "Union Sulphur Company" has been so successful that it has acquired the whole of the trade of the United States and also exports considerable quantities. The production amounts to several hundred thousand tons per annum.

The sulphur as it comes up from the well is said to have a purity of 99·98 per cent. It is simply run into great bins, which hold as much as 150,000 tons each. When it has cooled the sides of the bins are removed, the sulphur is broken up, and is then ready for shipment.

The Anglo-Sicilian Sulphur Company finding itself unable to contend with Frasch's Company finally retired from the business, but it had made enormous profits for many years. The Italian Government has formed a compulsory trust to control the marketing of Sicilian sulphur and ensure a living wage to the Sicilian workmen. This has proved very successful and the workers in Sicily are now better off than they have been for many years past.

On the occasion of the presentation to him of the Perkin Medal, Frasch gave a very interesting account of the various difficulties he had to contend with in working out his invention, and this is published in the *J.S.C.I.*, 1912, pp. 168–176.[1]

[1] *See also S.S.* 1911, p. 236.

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CHAPTER VI

MANUFACTURE OF GUNPOWDER

Advantages and disadvantages : Composition : Grinding the ingredients : Weighing and mixing : Incorporating or milling : Automatic drenchers : Removing the mill-cake : Breaking down : Pressing : Granulating or corning : Dusting and glazing : Stoving or drying : Finishing and blending : Cut powders : Moulded powders : Products of explosion : Blasting powders : Sprengsalpeter : Cahuecit : Petroklastit : Bobbinite : Water-soluble powder

THE invention of so many other blasting explosives and smokeless powders has greatly restricted the consumption of black powder, but it has been able to hold its own in certain fields in consequence of its advantages : its low price, the ease with which it can be ignited, its insensitiveness to shock, its stability at moderately high temperatures, its regular rate of burning, and the non-corrosive nature of the residue that it leaves in the gun. But against these must be placed its great disadvantages : its want of power and the great quantity of smoke that it evolves. For shot-guns its rate of explosion is suitable, only the recoil and smoke are disagreeable, but for rifles the rate of burning cannot be controlled sufficiently ; for driving the bullets out of shrapnel shell there is no better explosive, and it is still used for armour-piercing shell, because the high explosives used for other sorts of shell will not withstand the great shock of impact without exploding prematurely ; for filling the rings of time fuses for shell no satisfactory substitute has yet been found.

Guttmann, in his book on the *Manufacture of Explosives*, published in 1895, gave the following as the compositions of the principal powders made at that time : **Composition.**

	Saltpetre	Sulphur	Charcoal
(*a*) *Rifle Powders :*			
Austria-Hungary	75	10	15
Belgium	75·5	12	12·5
China	75	10	15
France	75	10	15
Germany [1]	74	10	16

[1] The proportions afterwards used in Germany for rifle powder were 75 : 9 : 15.

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	Saltpetre	Sulphur	Charcoal
(*a*) *Rifle powders:*			
Great Britain	75	10	15
Holland	70	14	16
Italy	75	10	15
Persia	75	12·5	12·5
Portugal	75·7	10·7	13·6
Russia	75	10	15
Spain	75	12·5	12·5
Sweden	75	10	15
Switzerland	75	11	14
Turkey	75	10	15
United States	75	10	15
(*b*) *Cannon Powders:*			
Austria-Hungary	74	10	16
France	75	10	15
Germany	74	10	16
Great Britain	75	10	15
Switzerland	75	10	15
(*c*) *Sporting Powders:*			
Austria-Hungary	76	9·4	14·6
France	78	10	12
Germany	78	10	12
Great Britain	75	10	15
Switzerland	78	9	13
(*d*) *Blasting Powders:*			
Austria-Hungary	60·2	18·4	21·4
France	72	13	15
Germany	70	14	16
Great Britain	75	10	15
Italy	70	18	12
Russia	66·6	16·7	16·7

Blasting powders, however, vary in composition far more than this Table indicates, powders with different rates of burning being used for rocks of different degrees of hardness. Thus the French Government factories make three sorts of mining powder:

	Saltpetre	Sulphur	Charcoal
Ordinary Powder	62	20	18
Slow Powder	40	30	30
Strong Powder	72	13	15

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The powders manufactured in Belgium have the following compositions :

	Saltpetre	Sulphur	Charcoal
Rifle Powder	75	12·5	12·5
Cannon Powder	75	12·5	12·5
Sporting powder	78	10	12
Blasting powder	75	12	13
Slow Powder or Pulvérin . . .	70	13	14 & 3% wood meal
Slow Powder in cartridges . . .	70	13	14 & 3% dextrine
Export powder	68	18	22

In France " pulvérin " is also prepared for the manufacture of fireworks; it contains : saltpetre 75·0, sulphur 12·5, charcoal 12·5, simply mixed together.

Grinding the ingredients.

Before they are mixed together the three ingredients are powdered. As they are not explosive when separate, they can be ground up in any suitable mill. In this respect, however, some reserve must be made as regards the sulphur : this has a great tendency to become electrified, and as it is also very inflammable an electric spark may easily set it alight or cause the explosion of a mixture of sulphur-dust and air. Rapid-moving machinery is therefore to be avoided ; the parts should all be made of metal and " earthed." In some works the sulphur is mixed with a small proportion of the saltpetre before grinding to prevent this electrification, which has the further disadvantage that it causes the sulphur to cake together and so escape proper grinding. At Waltham Abbey the sulphur is ground under steel-edge runners similar to those used for incorporating the powder.

The charcoal is generally ground in a machine resembling a large coffee mill (*see* Fig. 4), but in some factories ball-mills are used, the charcoal being placed in a drum with bronze balls. The drum is then rotated until the constant falling of the balls on to the charcoal has reduced it to a sufficiently fine state of division.

Sulphur and saltpetre may also be ground in the Excelsior mill, but if the saltpetre is already in fine crystals it need not be ground, but only sifted.

Weighing and mixing.

The three ingredients are carefully weighed out, preferably each in separate scales. An extra amount of saltpetre is often taken to allow for the moisture in it, the actual proportions weighed out being sometimes 76·0 . 15·0 : 10·0 instead of 75·0 : 15·0 : 10·0. But the charcoal usually contains quite as high a percentage of moisture as the saltpetre. It is not surprising therefore that analysis sometimes shows a percentage of charcoal which is below the theoretical.

The ingredients are then given a preliminary mixing. In Germany this is done in a rotating drum with lignum vitæ balls. The drum is made of wood and may be lined with leather ; iron must be avoided in its construction ;

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the axle must be covered with leather. At Waltham Abbey the mixing is done in a cylindrical drum of copper or gun-metal about 18 inches long and 2 feet 9 inches in diameter. Through the centre passes an axle carrying eight rows of fork-shaped arms, called "flyers." The drum rotates in one direction making 40 revolutions per minute. The axle moves in the other direction and makes 120 revolutions per minute. The ingredients are mixed for five minutes, and then sifted through a fine-mesh sieve of copper or brass wire. The sifting at this stage is very important, as any hard particles left in the charge are likely to cause an explosion in the incorporating mill. For this reason the sifting is sometimes done by hand. The "green" charge is now placed in a waterproof bag ready to be taken to the incorporating mill.

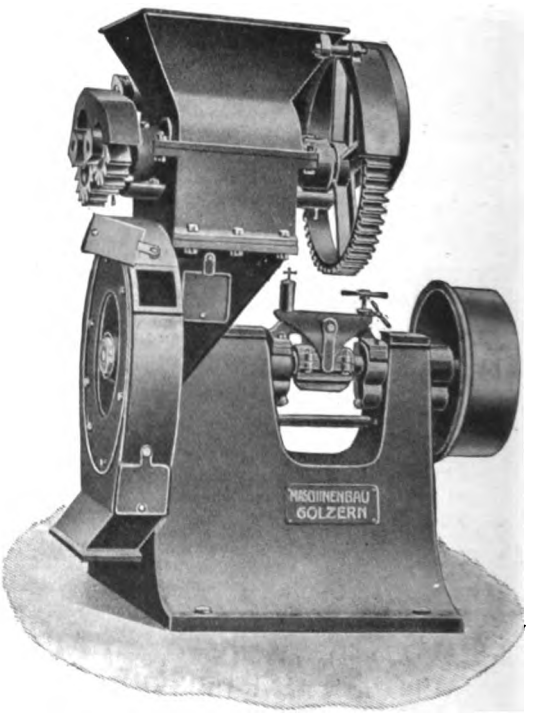

FIG. 4. Excelsior Mill, made by Maschinenbau A.-G. Golzern-Grimma

Incorporating or milling.

On the Continent stamp-mills are still used to a small extent for incorporating as well as mixing gunpowder. In Germany the stamp-heads may be made of copper, zinc, bronze or other suitable alloy. The charge is placed in a spherical hole in a block of wood, with a piece of specially hard wood inserted at the bottom for the stamp to play upon. The stamping is carried on for about fourteen hours. If continued longer the density of the powder diminishes and the ballistics deteriorate.

In England, however, incorporating mills are always used. Formerly these consisted of two heavy stone edge-runners working on a stone bed-plate. Now it is more usual to use iron runners working on an iron bed-plate; of course iron must not work upon stone or vice versa on account of the danger of generating sparks. In the most usual type of mill the runners are 6 or 7 feet in diameter and about 15 inches wide, and weigh about 4 tons each. They rotate on the opposite ends of a horizontal shaft, which is carried by a cross-head, which again is attached to a vertical shaft making about eight revolutions a minute. Usually the two edge-runners are mounted at different

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distances from the central shaft so that one works the outer part of the charge and the other the inner, but their paths overlap. There are two ploughs of wood covered with leather, which are fixed to the shaft and travel round with it. These continually push the charge away from the centre and the curb respectively, and bring it under the edge-runners again.

In the Gruson mill (Fig. 5) the iron runners do not rest on the bed but are suspended a short distance above it, so that there is no danger of a very thin layer of powder being subjected to great friction. The bearings are so suspended that either runner can travel upwards independently of the other when an extra thick portion of charge comes underneath it. The runners weigh about $5\frac{1}{2}$ tons each and rotate equidistantly round the main vertical shaft. The ploughs are made of phosphor bronze, and each runner is also provided with a scraper to prevent the charge being thrown off the bed. The drive is by means of a large bevelled gear-wheel, which may be arranged either above the machine or below it.

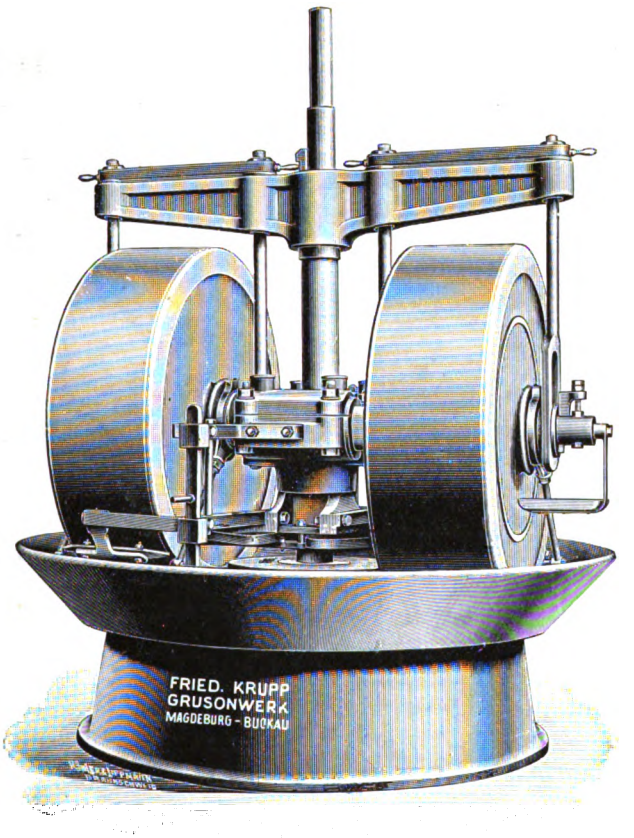

FIG. 5. Gruson Gunpowder Mill

In Germany iron runners are not allowed to work on an iron bed-plate unless they are suspended as in the Gruson mill. If they actually rest upon the bed, it must be made of wood fastened down with brass screws.

By the action of the runners the ingredients are crushed and ground together very intimately without subjecting the mixture to any violent action.

Usually about six incorporating mills are arranged in a row and driven from a common shaft actuated by a single water-wheel or steam-engine. Each mill is separated from the next by a strong masonry wall. Explosions in these mills

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are fairly frequent in spite of every precaution, but as a rule no very serious damage is done. In 1907 there were nine such explosions in England, but only one man was injured; in 1908 there were five explosions and two men were injured; in 1909 there were seven explosions and no men were injured. The reason why there are so few men killed or injured in these accidents is that as a rule there is no one in the mill house: after the charge has been started the man in attendance goes on to see to other mills and only comes occasionally to see that all is right and to add a little water to the charge if necessary. In Germany no workman is allowed to remain in the building whilst the mill is working at full speed.

A charge consists of 60 to 80 lbs., the time of incorporation varies with the description of the powder: the longer the incorporation the faster the powder burns. Cannon powders are usually milled for three or four hours,

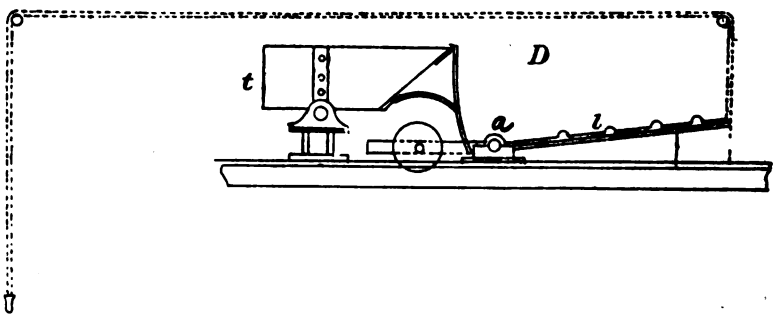

FIG. 6. Drenching Arrangement for Powder Mills

rifle powders eight, and sporting powders as much or more. The charge must be kept moist the whole time; for this purpose the mill-man adds water from time to time, preferably condensed water from a steam trap. Formerly urine was frequently used instead of water. For fine grain powders 1½ to 3 per cent. of moisture should be present in the finished mill-cake, for larger sizes 3 to 6 per cent.

Automatic drenchers.

In order to prevent the explosion in one mill being communicated to the other mills of the group, each one is provided in England with an automatic drenching arrangement (*see* Fig. 6). This consists of a lifting board *l*, provided with a counterpoise weight. There is also a tank *t* full of water, supported on a hinge and a leg at one end that rests on a projection from the lifting board. When the latter is lifted, the leg is released, the tank tips forward and the water is poured over the charge in the mill. The axle *a* is common to all the lifting boards of the group of mills, so that if there be an explosion in one of the mills the corresponding board *l* is raised, taking with it all the other similar boards, and all the charges in the group are drenched and so

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rendered unexplosive. In order to make the mechanism sufficiently sensitive it is important that the boards be not too small and not too near the roof, and that they be directly over the mills. The second point is essential, because if the board be very near the roof a reflected wave of pressure reaches it almost immediately after the direct wave and before the mechanism has had time to act.

Removing the mill-cake.

The mill-cake often becomes caked on to the bed very firmly. Many accidents having been caused by removing this with metal tools, H.M. Inspector of Explosives issued a letter on December 27, 1883, proposing the adoption of the following special rule in all black powder works :

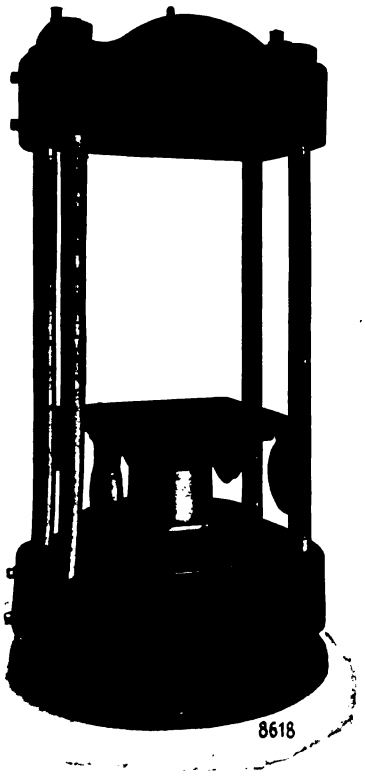

FIG. 7. Gunpowder Press

"Whenever it may become necessary in mills or other buildings to remove any powder incrustations (whether from the machinery or elsewhere), which cannot be easily brushed off, such removal is to be effected without the use of any metal tool whatever ; the hard powder is to be removed by means of water, supplemented, if need be, when the whole incrustation has been thoroughly saturated, by a suitable wooden instrument gently applied."

Breaking down.

The mill-cake is next reduced to a rough powder by hand or by passing it through gun-metal rolls in a machine somewhat resembling the granulating machine, but simpler.

Pressing.

Then the mixture is subjected to high pressure in a press. This converts it into a hard mass, the constituents of which have no tendency to separate again from one another, and also increases the density of the powder. Formerly the powder was compressed in a very strong box, but this is no longer done on account of the dangerous friction against the sides.

For moulded powders and blasting cartridges special presses are used, which will be described later. Granulated powders are pressed in presses of the type shown in Fig. 7. The mill-cake is built up on a small trolley : first a plate of copper, bronze, or ebonite is put down, and a temporary frame put round it, then a layer of the mill-cake about $\frac{3}{4}$-inch thick is carefully spread, then another plate and another layer of powder, until about 10 cwt.

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of mill-cake has been built up with about twenty plates. The temporary frames are then removed and the trolley is wheeled on to the press, and the pressure is gradually applied. The amount of compression required varies with the amount of moisture in the mill-cake and the density to be attained in the finished powder. For a mixture containing about 3 per cent. of moisture it is necessary to apply a pressure of about 400 lb. per square inch of plate surface for 1½ to 2 hours to obtain a density of 1·7. The amount of compression is measured by the motion of the press rather than by the hydraulic pressure; this motion may be 24 or 30 inches according to the dimensions of the press, etc. The pressure is usually released and reapplied several times to obtain a satisfactory result.

Ebonite plates are sometimes preferred to metal because they keep their shape better and yet give sufficiently to transmit the pressure evenly. If the cake be very dry the ebonite may become electrified, however, and so produce very dangerous sparks. In Germany the use of ebonite plates is forbidden, and cloths are laid between the plates and the powder. The four columns of the press should be made of mild steel with an ample margin of strength even if the whole pressure is borne by only two of them. They may with advantage be covered with leather. It was recommended by H.M. Inspector of Explosives [1] that the press should not be worked directly off the hydraulic pump, but from an accumulator, and that the drive of the pump should not be positive, but by friction.

The explosion of a press-house is more destructive than that of any other building in a black powder works, as might be expected, considering that there is about half a ton of powder in one mass strongly compressed. The house should therefore be specially well isolated from other buildings by mounds, etc. In some works the workmen are not allowed to be in the press-house whilst the pressure is on the powder; the pressure can be applied and controlled from another compartment, where there is also an indicator showing the position of the platform of the press.

When sufficiently pressed the pressure is released and the trolley is wheeled away, and the press-cake removed from it by hand or with wooden tools. The outer portion of each slab is rejected as it is not sufficiently compressed; it is added to a later pressing.

Blasting powder is sometimes compressed between rollers.

Granulating or corning.

The broken-up press-cake is put in barrels and taken to the granulating or corning house. Here there is a machine having three or four pairs of gun-metal rolls, through which the press-cake is passed, and a number of automatic sieves, which sort out the grains of the required size (*see* Fig. 8). The top pair of rollers usually has pyramidal teeth: from this the material passes over a sieve to the next pair of rolls, which has smaller teeth. The lowest

[1] Special Report No. 138.

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pair are plain. The pieces that are not fine enough are passed through the machine again; the dust and fine powder are milled for a short time and pressed again. The bearings of one or both rolls of each pair are provided

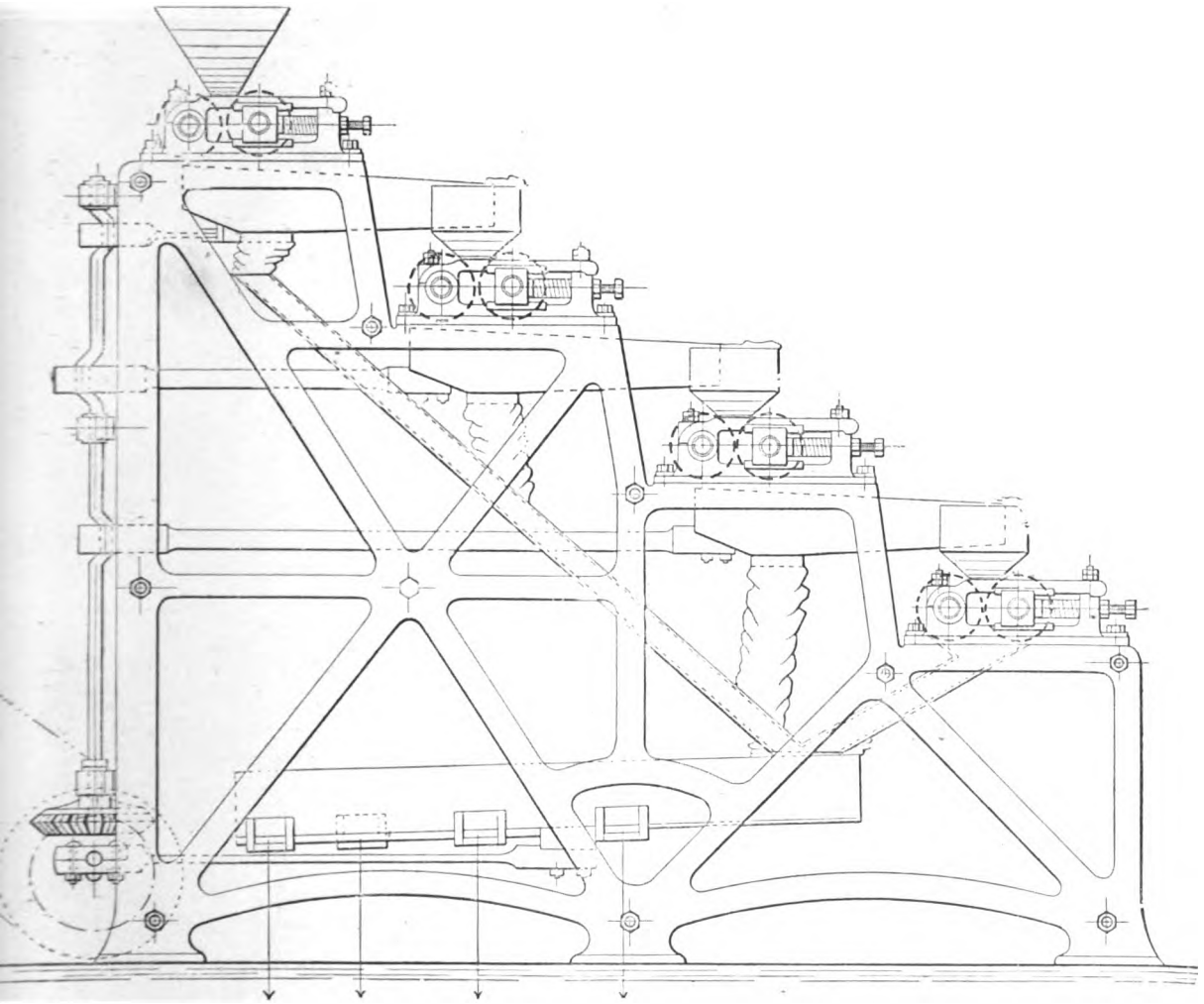

FIG. 8. Corning Machine, made by Maschinenbau A.-G. Golzern-Grimma

with springs or weights to keep them in position, and are not rigidly fixed. Consequently if an extra hard piece of cake passes through the rolls it is not subjected to great violence: the rolls give way and the piece passes through.

This type of granulating machine was invented in 1819 by Colonel Congreve,

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and is the one in most general use. Various other types have been tried, but none produces such a good angular grain.

Dusting. Powders made with dog-wood charcoal produce a lot of dust in the corning process, and it is best to remove this by passing the powder through a dusting reel. This is simply a cylindrical reel set at an angle of about 4° to the horizontal and covered with fine woven wire of copper or brass. It is open at both ends and rotates on its axis, making about forty revolutions per minute. The powder is simply passed through this and caught again in a barrel.

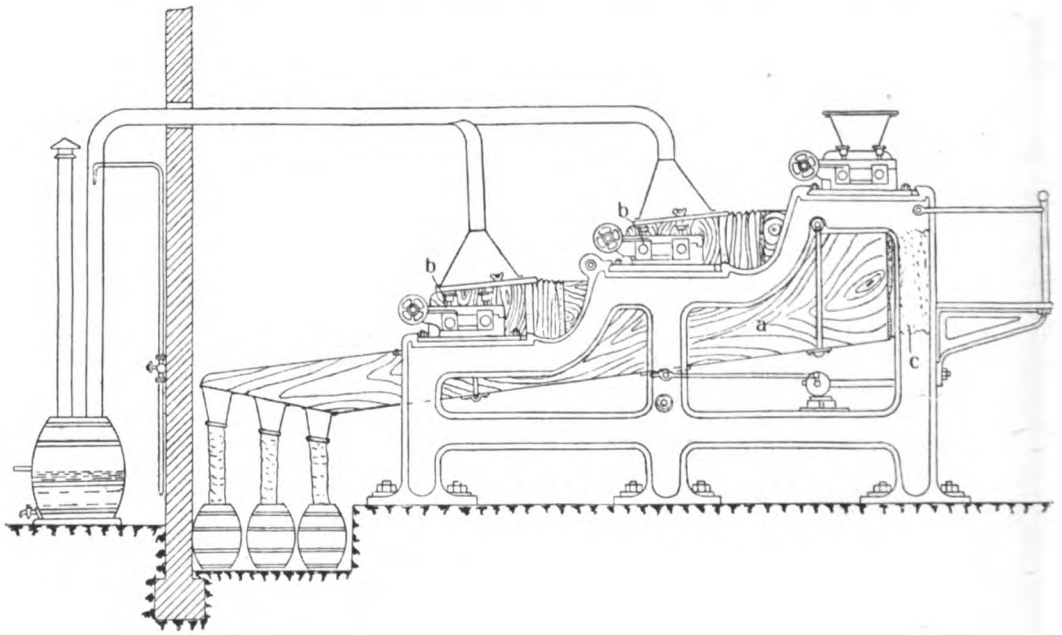

FIG. 9. Corning Machine with Dust-Remover

Glazing. The glazing operation is carried out in wooden drums, which rotate on their axis about thirty times a minute. Cannon powders receive an addition of a small proportion of graphite and are glazed for two or three hours. Rifle and sporting powders, and others that are required to burn quickly, do not receive any graphite, but are glazed longer.

Stoving or drying. The stove may be heated either by forcing hot air through it, or by arranging hot water or steam pipes in it. The easiest and most economical method is to dry with steam, and as black powder is not very sensitive and is not liable to spontaneous decomposition, this method is usually adopted. Only low-pressure steam should be used, the exhaust being open to the air. The powder is placed on canvas trays supported on wooden racks. Inlets and outlets are provided for the air, and the temperature is kept at about 40° C. (104° F.).

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The time required to dry the powder varies from one to four hours according to the size of grain.

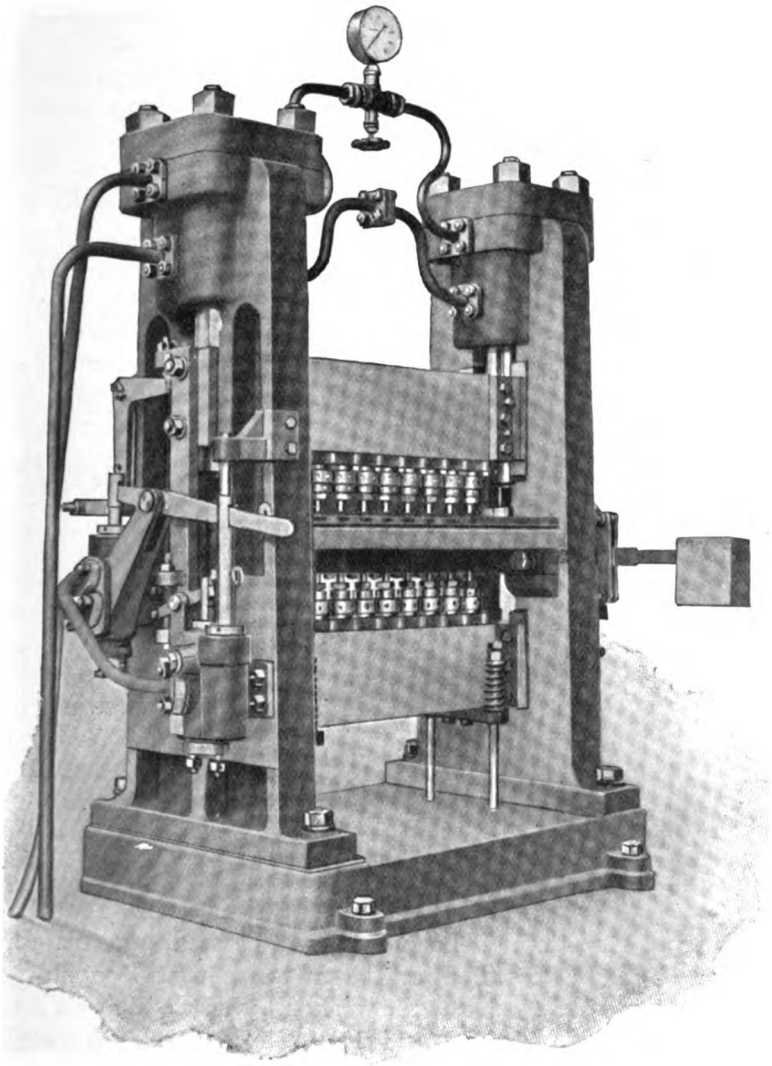

FIG. 10. Hydraulic Automatic Press for Moulded Powders and Blasting Cartridges (Maschinenbau A.-G. Golzern-Grimma)

Finishing and blending.

To remove the last traces of dust and give the powder a good "colour" it is now treated for some two hours in the finishing reel, which is covered with fine canvas, and finally thoroughly blended into large uniform batches.

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The last operation is performed at Waltham Abbey by pouring it into a hopper, which is provided with four delivery shutes, so that the contents of the hopper are divided into four equal portions. By repeating this operation in a systematic manner the desired object is attained very effectually.

Cut powders. Powder for cannon of large size, 6 to 12-inch bore, was made by cutting the press-cake into cubes. The slabs from the press were passed under a roll armed with longitudinal knives, whereby the cake was cut into strips, and these were then passed under another similar roll in the other direction and so cut into cubes. The glazing, stoving, finishing and blending were very much as for granulated powder, except that the stoving had to be continued for about thirty hours at 55° C. These cut powders are but little made now, as they have been displaced by smokeless powders.

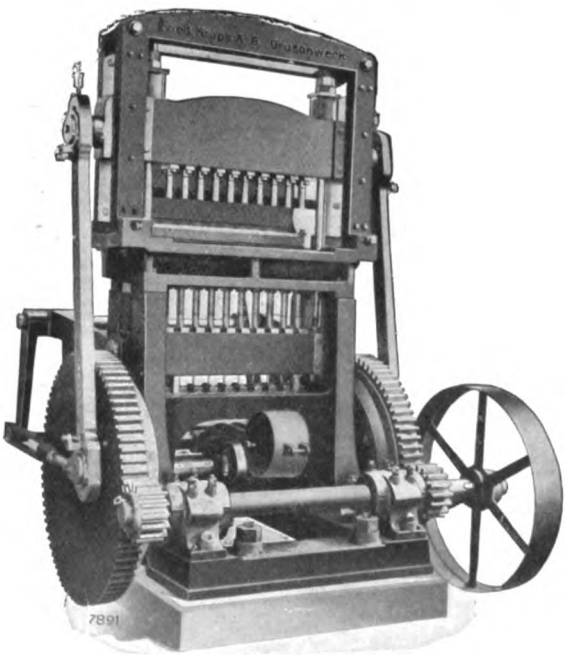

FIG. 11. Mechanical Press for Moulded Powders, &c. (F. Krupp A.-G. Grusonwerk)

Moulded powders. Moulded powders also are but little used for the same reason, but much the same process is used for making moulded cartridges of mining powder, and also pellets for time and percussion fuses and for other ammunition. The general form of all these articles is practically the same: a hexagonal or round cylinder with a central perforation. The powder is pressed, granulated, dusted and blended as already described, and then taken to the moulding house. Two different types of press are used, worked by hydraulic and mechanical pressure respectively (*see* Figs. 10 and 11). The general principle is, however, the same. The granular powder is put into a hopper and flows from there into a measure that automatically measures off the right quantity, which then passes into the die. The dies are arranged in rows in a plate, so that whilst one row is being filled another is being pressed. The pressure is usually applied simultaneously from above and below by two different plungers. The central hole is formed by means of a pin which passes through the lower plunger and into the other. Hydraulic presses are safer, but

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mechanical ones more rapid in their action. For blasting cartridges machines are also made with rotating tables containing a number of dies : each operation, filling, pressing, removing, is performed at a different position of the table. Such machines are quite automatic and require very little attention.

Both black and brown powders have been moulded into prisms which are usually 25 mm. high and 40 mm. wide, measured across the corners of the hexagons. The following Table gives the details of the English and German powders :

Country	Name	Charcoal	Proportions	Density
England	Prism[1] Black	Black	75 : 10 : 15	1·76
„	Prism[1] Brown	Brown	79 : 3 : 18	1·80
„	E.X.E.	„	77·4 : 5 : 17·6	1·80
„	S.B.C.	„	79 : 3 : 18	1·85
Germany	P.P.C./68	Black	74 : 10 : 16	1·66
„	P.P.C./75	„	74 : 10 : 16	1·76
„	P.P.C./82	Brown	78 : 3 : 19	1·86
„	P.P.C./85	„	80 : 0 : 20	1·88

P.P.C/68 has seven holes, all the others, English and German, only one. The value of the brown straw charcoal is that under the high pressures it flows and holds the mixture together, making it into an impervious mass, which can only burn at the surface, whereas black powders have slight pores through which the flame can penetrate. This may be seen by examining the powders under the microscope.[1]

Products of explosion.

The products formed on the explosion of various gunpowders under various conditions were determined by Noble and Abel.[2] The mean percentages from R.L.G. Powder were :

Gases	42·98%
Solids	55·91
Water	1·11

Gases, per cent. by volume		Solids, per cent. by weight	
Carbon dioxide	49·3	Potassium carbonate	61·0
Carbon monoxide	12·5	Potassium sulphate	15·1
Hydrogen	2·2	Potassium sulphide	14·5
Methane	0·4	Potassium sulphocyanide	0·2
Nitrogen	32·9	Potassium nitrate	0·3
Sulphuretted Hydrogen	2·6	Sulphur	8·7

From 1 g. of the powder 271·3 c.c. of gas were produced, measured at 760 mm. and 0° C., and the quantity of heat liberated was 700·7 calories (*see also* p. 378).

[1] *See* Cronquist, *S.S.*, 1906, p. 53.

[2] *Trans. R.S.*, 1875 and 1879.

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Blasting powders.

The usual composition of black blasting powders has already been stated (p. 62). The violence of the powder can be varied by altering the composition, the density or the size of the grains : the powder is made slower by diminishing the percentage of saltpetre, compressing to a higher density or making

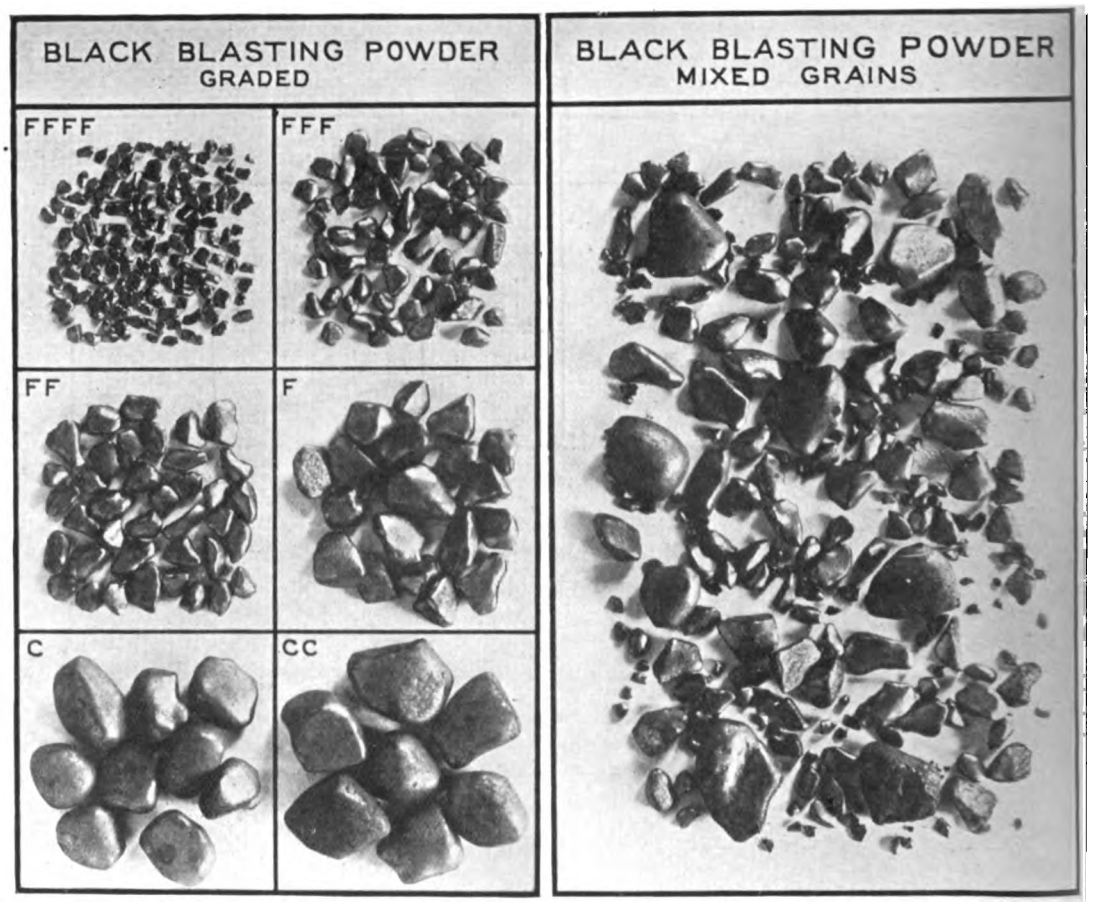

FIG. 12. American Black Blasting Powders (Munroe and Hall)

the grains coarser. In France the mining powders manufactured in the State mills are incorporated, not under edge-runners, but in copper drums with wooden and bronze balls, and the granulation is also effected in drums with the aid of a spray of water.

In America enormous quantities of blasting powder are used containing sodium nitrate (Chili saltpetre) instead of the potassium salt. This burns more slowly than ordinary gunpowder, but is more powerful, as it evolves

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a greater volume of gas and more heat, but its principal advantage is its low price, for it is used for many purposes where in Europe hand labour would be employed. According to Chalon,[1] the composition varies between the following limits :

		Mean
Sodium nitrate	67·3 to 77·1	74
Sulphur	9·4 to 14·3	10
Charcoal	22·9 to 8·6	16

The usual proportions in this " black blasting powder " are given by Munroe and Hall [2] as 73 : 11 : 16. The incorporation is not so thorough as in the case of ordinary black powder, and the charcoal is generally obtained from coarser-grained woods. As the sodium nitrate is hygroscopic, care must be taken not to expose the powder to damp air more than can be helped. The following are the sizes of American black blasting powders :

	Diameters of round holes in screens in $\frac{1}{64}$th inches	
	Through which grains pass	On which grains collect
CCC	40	32
CC	36	24
C	27	18
F	20	12
FF	14	7
FFF	9	3
FFFF	5	2

The following blasting explosives resembling black powder in composition are made in Germany, and are allowed to be sent as goods in unlimited quantities, as they are considered safer to handle than ordinary black powder :

Sprengsalpeter.

" Sprengsalpeter " (blasting saltpetre) is a mixture of sodium nitrate, sulphur and brown coal in about the proportions 75 : 10 : 15, and is very largely used in the Stassfurt salt-mines where the soft and brittle nature of the salts, such as carnallite, require an explosive that is milder than ordinary blasting powder. It possesses the advantage of being cheap and not giving rise to poisonous fumes. Harder materials, such as sylvinite and rock-salt, are blasted with a combined charge of nitro-glycerine explosive and Sprengsalpeter.

Cahuecit.

" Cahuecit " was invented by R. Cahuc some forty years ago and was manufactured at one time at Dartford under the name of Safety Blasting Powder or Carboazotine. It had the composition :

Saltpetre	64
Sulphur	12
Lamp-black	7
Bark or wood-pulp	17

[1] *Les Explosifs Modernes*, 3rd ed., 1911, p. 264.

[2] *Primer on Explosives for Coal Miners*, Washington, 1911, p. 16.

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to which was added 1 to 5 per cent. of sulphate of iron. After mixing the ingredients roughly in a drum they were introduced together with a considerable bulk of water into a steam-jacketed pan where the mixture was heated with constant stirring until almost dry. The mixture was imperfect in consequence of the tendency of the soluble salts to crystallize out.[1] It is still manufactured in Germany, and has been found good for blasting basalt.[2] The official German definition is: a compressed mixture of not more than 70 per cent. saltpetre, 8 per cent. lampblack, about 12 per cent. flowers of sulphur, at least 10 per cent. cellulose, and a small quantity of iron sulphate.

Petroklastit. "Petroklastit" (Haloklastit) has approximately the following composition:

Sodium Nitrate	69
Potassium nitrate	5
Sulphur	10
Coal tar pitch	15
Potassium bichromate	1

Its strength and sensitiveness as compared with black blasting powder[3] are:

	Trauzl test	Falling weight
Petroklastit	157	100
Black powder	108	65

Its official definition is: a compressed mixture of sodium nitrate, sulphur, coal-tar pitch, saltpetre, and not more than 1 per cent. potassium bichromate, also with an addition of not more than 10 per cent. charcoal. It has been used in stone quarries and potash mines.

Bobbinite. In English coal-mines the most largely used explosive has been Bobbinite, which is a black powder mixture with an addition of the sulphates of copper and ammonium, or of starch and paraffin-wax. It is the only explosive of this class that was able to pass the Woolwich test for "Permitted Explosives"; it does not pass the Continental and Rotherham tests. In 1906 a Departmental Committee was held at the Home Office to inquire whether this explosive should be removed from the list. This has not been done, but by the Explosives in Coal-Mines Order of September 1, 1913, its use has been restricted to mines that are not gassy or dusty. In these its use is permitted for a period of five years from January 1, 1914. The following is its composition according to the official definitions, and an analysis made by Hall and Howell:[4]

[1] Guttmann, *Manufacture*, vol. i., p. 273; *see also* Cundill and Thomson, p. 142.
[2] *S.S.*, 1908, p. 97.
[3] Zschokke, pp. 42, 57.
[4] U.S. Bureau of Mines, *Bull.* 15, 1912, p. 179

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	Official definitions		Hall and Howell
	First	Second	
Nitrate of potassium	62·0–65·0	63·0–66·0	65·31
Charcoal	17·0–19·5	18·5–20·5	19·52
Sulphur	1·5– 2·5	1·5– 2·5	2·63
Sulphate of ammonium \ Sulphate of copper /	13·0–17·0	—	—
Rice or Maize starch	—	7·0– 9·0	8·73
Paraffin wax	—	2·5– 3·5	3·35
Moisture	0·0– 2·5	0·0– 3·0	0·46

Water-soluble powder.

Raschig proposes to make a cheap blasting powder consisting of 65 per cent. sodium nitrate and 35 per cent. sodium cresol-sulphonate. These are dissolved in water and the solution is evaporated very rapidly on a rotating drum heated by high-pressure steam. It is claimed that the expensive and dangerous operation of incorporation is thus done away with. It is necessary to select a combustible constituent like the cresol-sulphonate, that has a high solubility of the same order as the nitrate, otherwise there would be a tendency for the substances to separate during the evaporation. Safety explosives containing ammonium nitrate instead of the sodium salt have been registered under the name of "Raschit." [1]

[1] *See* Ang. 1912, p. 1194 ; Ger. Pat. App. R. 54,360 of 3/2/12 ; *S.S.*, 1912, p. 292.

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PART III

ACIDS

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CHAPTER VII

SULPHURIC ACID

Manufacture : Concentration : Melting-points : Specific gravities : Calculations

THE manufacture of sulphuric acid is treated fully in special works such as Lunge's *Sulphuric Acid and Alkali*. Here only the general principles can be dealt with and those special features which are of importance to the manufacturer of explosives. **Manufacture.**

Until the end of the last century, or the beginning of this, practically all the sulphuric acid was made by the "chamber process." Now very large quantities are produced by the "contact process." In both processes the first stage is to burn sulphur, or a sulphur ore such as zinc-blende or pyrites, in an excess of air, thus producing a gaseous mixture consisting mostly of oxygen, nitrogen, and sulphur-dioxide. It is necessary now to make the sulphur-dioxide combine with a further quantity of oxygen. In the chamber process this is done by mixing a small proportion of oxides of nitrogen with the gases and water in the form of spray or steam. Various intermediate products are formed, but the final product is "chamber acid," containing about 70 per cent. sulphuric acid and 30 per cent. water, or "Glover tower acid," containing about 80 per cent. acid.

In the contact process the sulphur-dioxide is made to combine with oxygen to form the trioxide, SO_3, by passing the gases over a heated contact substance, such as platinum or iron oxide. No steam or spray of water is introduced, and consequently it is not necessary afterwards to concentrate the acid to bring it up to a high strength, as is the case with the chamber process. On the contrary the sulphur-trioxide has to be absorbed in weak sulphuric acid so as to obtain an acid of convenient strength. Very great difficulties were experienced at first because after a short time it was found that the spongy platinum used as the contact material ceased to be active. It was discovered, however, that this was due to the presence in the gases of traces of impurity, such as arsenic, which "poisoned" the platinum. When these are entirely removed the contact material retains its activity for a long time. The principal motive of the inventors in working out the contact process was to produce at a reasonable cost a fuming acid for use in the manufacture of artificial

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indigo, but large quantities of strong acid are also required in the explosives industry, and some explosives works have in fact erected contact plants of their own.

In the burners pyrites is generally burnt, but sometimes blende. The burnt pyrites or blende is afterwards sent to smelting works, where the metal is extracted. Sulphur (brimstone) is used only in localities where there are no smelting works available.

Concentration. Acid from the chamber process requires to be concentrated before it can be used for most of the purposes of the explosives industry. Sulphuric acid that has been recovered from the waste acid by denitration has much the same strength as that from the chamber process and also requires reconcentration. Those works that have a contact sulphuric acid plant can use this recovered acid to absorb the sulphur-trioxide, and so bring it up to any required strength. In factories where the acid is purchased the same object can be accomplished by mixing the weak recovered acid with fuming acid (N.O.V.) [1] containing 20 or 60 per cent. anhydride. But in some processes of manufacture as, for instance, the displacement process for gun-cotton, such large quantities of weak acid are produced that reconcentration is necessary. Such reconcentration is nearly always carried out in the explosives works themselves, as it does not pay to transport such a material backwards and forwards by road or rail.

Kessler's plant. The type of plant used almost universally in the explosives industry is that of Kessler, the principle of which is to bring a current of hot gas from a gas producer in contact with the acid in a plant constructed of volvic stone, which is only very slightly attacked by the hot concentrated acid. Fig. 13 shows an early form of the plant which has since been modified in some details. The hot gas from the producer enters by the tube *O* into the "saturex" *S*, where it passes down the channels *q*, and is caused by baffles to rush over the surface of the acid into the channels q^1. From here it passes up through the "plateaux" *A*, *B*, *C*, *D*, where the inverted cups cause it to bubble through the acid which passes down from one plateau to the other by means of the overflow pipes *n*. The acid thus receives a preliminary concentration, and the gas is partially cooled down before it goes through the dome *Z* and the pipe *P* to the condenser. The weak acid is introduced on the top plateau, and the concentrated acid flows out of the saturex through the pipe *m* into a lead tank, where it is cooled by means of a coil through which water flows. The arrangement of the baffles in the saturex has now been altered; they run transversely to the direction of flow of the gas and acid, and the hot gas passes under each of them in turn.

[1] The commercial term for sulphuric acid of 92 to 96 per cent. strength (s.g. 1·83–1·84) is C.O.V. (concentrated oil of vitriol), that of the fuming acid containing anhydride is N.O.V. (Nordhausen oil of vitriol) or oleum.

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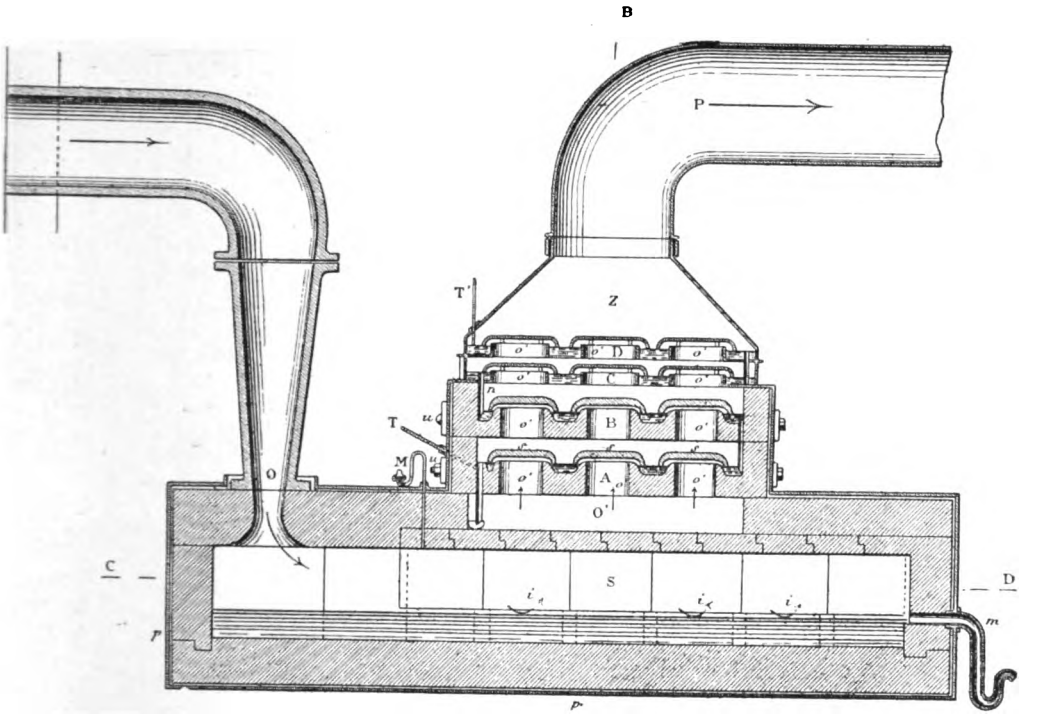
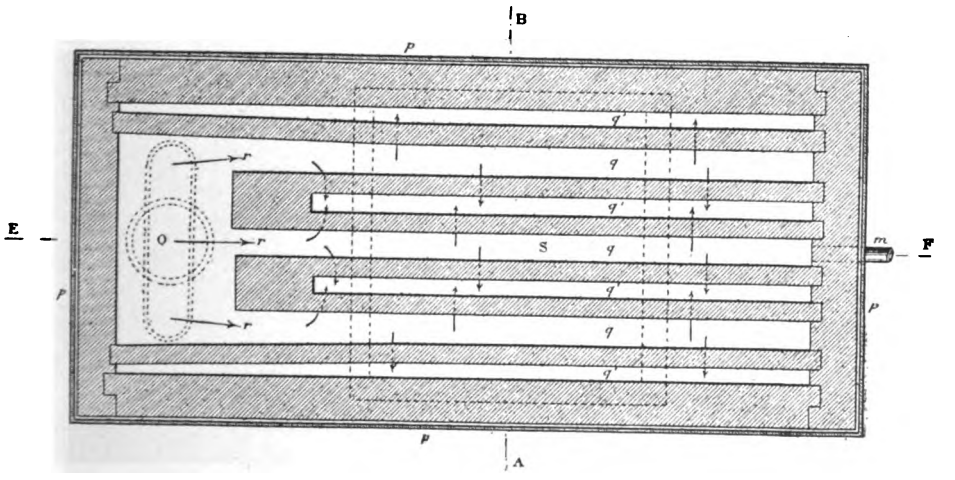


Sectional Elevation



Sectional Plan

FIG. 13. Kessler Concentrator

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The gas passing away through *P* carries with it a considerable amount of sulphuric acid, mostly in the form of very fine mist, which is very difficult to remove and is very injurious to the surroundings. The gas is therefore passed through a condenser consisting of a large lead tank packed with carefully graded cake. Formerly the gas was drawn off by means of a steam injector in the pipe *P*, but this was very extravagant in steam and caused the condensed acid to be very dilute. Now a fan is used instead. Water is sprayed into *P* to assist the condensation of the acid. The general arrangement of the plant is shown in Fig. 14. Careful regulation of temperatures and draughts is necessary to ensure the best results.

Melting-points.

In deciding what strength of oleum it is best to use one of the properties that must be carefully considered is that of the melting-points of the acids. In Fig. 15 are given the values as determined by Knietsch and published by him in the important paper on

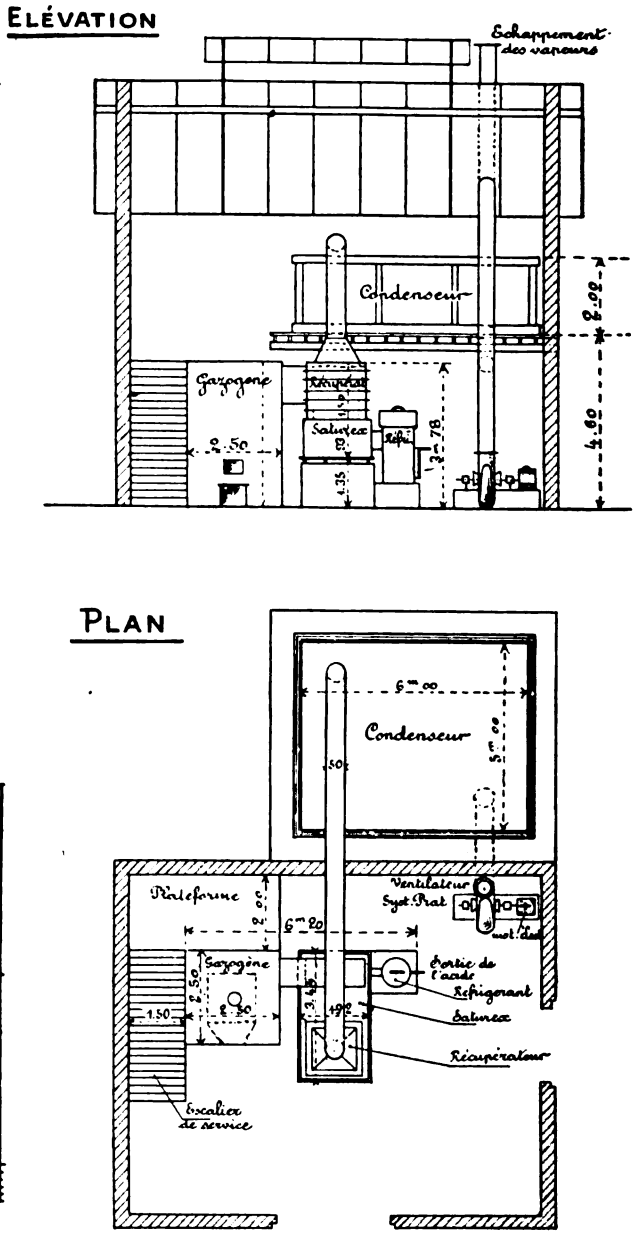
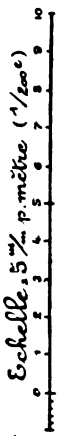


FIG. 14. Arrangement of Kessler's Plant for the Concentration of Sulphuric Acid



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the contact process, which he read before the German Chemical Society in October 1901.[1] It will be seen that there are maxima at the points corresponding to (H_2SO_4, H_2O), (H_2SO_4), (H_2SO_4, SO_3) and (SO_3), and minima at intermediate points. A strength that is much used is one containing 18 to 20 per cent. anhydride: it has the advantage that it is liquid at all ordinary temperatures. With an increase of strength the melting-point rises rapidly until with 45 per cent. anhydride it reaches 36°, a temperature at which it is very inconvenient to deal with an acid that gives off dense fumes even at the ordinary temperature and boils below 90°. From here the melting-point falls again until with a strength of 60 to 65 per cent. anhydride an acid is obtained which is liquid in summer and can be easily melted at any time of the year. The choice of acid to be used therefore rests between C.O.V. and N.O.V. containing 18 to 20 per cent. and 60 to 65 per cent. anhydride. The decision must depend on the price at which the acids can be obtained and the facilities for reconcentrating or using the weak acids produced in manufacture. Where such facilities are deficient it is better to use the stronger oleum. Very little waste acid will then be produced. Otherwise most works prefer to use the 20 per cent. oleum. C.O.V. is now little used in explosives works for revivifying waste acids.

One of the disadvantages of the 20 per cent. oleum is that it attacks iron much more strongly than either C.O.V. or the 60 per cent. oleum.[2] On the other hand, the vapour tension of the weaker oleum is considerably smaller than that of the stronger. Whereas C.O.V. containing 98·5 per cent. H_2SO_4 boils at 317°, and 100 per cent. acid at about 270°, 20 per cent. oleum boils at about 140° and 60 per cent. at 60° C.

Specific gravities.

Tables of the specific gravities of mixtures of sulphuric acid and water have been published by various investigators. There are slight differences between the best of them, due principally to the difficulty of determining the strength of the acid with a very high degree of accuracy, and perhaps partly to the presence of traces of impurity in the material. The Tables of Lunge and his co-workers Naef and Isler are much used, but upon the whole the figures of Pickering seem to be the best. Many of the Tables are not directly comparable because the specific gravities have been taken at different temperatures or are referred to water at different temperatures; in some cases the gravities are corrected for air displacement and in others not. For general work it is best to weigh both the acid and water at the ordinary temperature and not to correct for air displacement, for the introduction of small corrections is not only troublesome but is liable to lead to error. Pickering's figures were therefore calculated by me to this basis,[3] and are given in the following Table:

[1] Ber., 1901, 4093; *Chem. Ind.*, 1902, p. 6.
[2] *See* Knietsch, *loc. cit.*
[3] J.S.C.I., 1903.

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SPECIFIC GRAVITIES OF SULPHURIC ACID AT 15°/15° C. IN AIR

Specific gravity	0	1	2	3	4	5	6	7	8	9
1·00	0·00	0·14	0·28	0·43	0·57	0·71	0·86	1·01	1·15	1·30
1·01	1·45	1·60	1 75	1·89	2·04	2·19	2·34	2·49	2·64	2·79
1·02	2·93	3·08	3·23	3·38	3·53	3·67	3·82	3·97	4·12	4·26
1·03	4·41	4·56	4·70	4·85	5·00	5·14	5·29	5·44	5·58	5·73
1·04	5·88	6·03	6·17	6·32	6·46	6·60	6·75	6·89	7·04	7·18
1·05	7·32	7·47	7·61	7·76	7·90	8·04	8·19	8·33	8·47	8·62
1·06	8·76	8·90	9·04	9·18	9·33	9·47	9·61	9·75	9·89	10·03
1·07	10·17	10·31	10·45	10·59	10·73	10·87	11·00	11·14	11·28	11·42
1·08	11·56	11·69	11·83	11·97	12·11	12·24	12·38	12·52	12·66	12·79
1·09	12·93	13·07	13·20	13·34	13.48	13·61	13·75	13·89	14·02	14·16
1·10	14·29	14·43	14·56	14·70	14·83	14·97	15·10	15·24	15·37	15·51
1·11	15.64	15·78	15·91	16·05	16·18	16·31	16·45	16·58	16·71	16·84
1·12	16·98	17·11	17·24	17·37	17·51	17·64	17·77	17·90	18·03	18·16
1·13	18·30	18·43	18·56	18·69	18·82	18·95	19·08	19·22	19·34	19·47
1·14	19·60	19·73	19·86	19·99	20·12	20·25	20·38	20·51	20·64	20·77
1·15	20·90	21·03	21·16	21·28	21·41	21·54	21·67	21·80	21·93	22·05
1·16	22·18	22·31	22·44	22·56	22·69	22·82	22·94	23·07	23·20	23·32
1·17	23·45	23·57	23·71	23·83	23·96	24·08	24·21	24·34	24·46	24·59
1·18	24·71	24·84	24·97	25·09	25·22	25·34	25·47	25·59	25·72	25·84
1·19	25·97	26·09	26·22	26·34	26·47	26·59	26·71	26·84	26·96	27·09
1·20	27·21	27·33	27·46	27·58	27·71	27·83	27·95	28·08	28·20	28·32
1·21	28·45	28·57	28·69	28·82	28·94	29·06	29·18	29·31	29·43	29·55
1·22	29·68	29·80	29·92	30·04	30·17	30·29	30·41	30·53	30·65	30·78
1·23	30·90	31·02	31·14	31·26	31·38	31·50	31·62	31·75	31·87	31·99
1·24	32·11	32·23	32·35	32·47	32·59	32·71	32·83	32·95	33·07	33·19
1·25	33·31	33·43	33·55	33·67	33·79	33·91	34·02	34·14	34·26	34·38
1·26	34·50	34·62	34·74	34·86	34·98	35·09	35·21	35·33	35·45	35·57
1·27	35·68	35·80	35·92	36·04	36·15	36·27	36·39	36·51	36·62	36·70
1·28	36·86	36·97	37·09	37·21	37·32	37·44	37·56	37·68	37·79	37·91
1·29	38·03	38·14	38·26	38·37	38·49	38·60	38·72	38·83	38·95	39·06
1·30	39·18	39·29	39·41	39·52	39·64	39·75	39·86	39·98	40·09	40·20
1·31	40·32	40·43	40·54	40·66	40·77	40·88	40·99	41·11	41·22	41·33
1·32	41·45	41·56	41·67	41·79	41·90	42·01	42·12	42·23	42·35	42·46
1·33	42·57	42·68	42·79	42·90	43·01	43·12	43·23	43·35	43·46	43·57
1·34	43·68	43·79	43·90	44·01	44·12	44·23	44·34	44·45	44·56	44·67
1·35	44·77	44·88	44·99	45·10	45·21	45·32	45·43	45·53	45·64	45·75
1·36	45·86	45·97	46·07	46·18	46·29	46·39	46·50	46·61	46·71	46·82
1·37	46·92	47·03	47·14	47·24	47·35	47·45	47·56	47·67	47·77	47·88
1·38	47·98	48·09	48·19	48·30	48·40	48·50	48·61	48·71	48·82	48·92
1·39	49·02	49·13	49·23	49·34	49·44	49·54	49·65	49·75	49·86	49·96
1·40	50·06	50·16	50·26	50·37	50·47	50·57	50·67	50·77	50·88	50·98
1·41	51·08	51·18	51·28	51·38	51·48	51·58	51·68	51·78	51·89	51·99
1·42	52·09	52·19	52·29	52·39	52·49	52·59	52·69	52·79	52·89	52·98
1·43	53·08	53·18	53·28	53·38	53·48	53·58	53·68	53·78	53·88	53·97
1·44	54·07	54·17	54·27	54·36	54·46	54·56	54·65	54·75	54·85	54·94

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SPECIFIC GRAVITIES OF SULPHURIC ACID AT 15°/15° C. IN AIR—*continued*

Specific gravity	0	1	2	3	4	5	6	7	8	9
1·45	55·04	55·14	55·24	55·33	55·43	55·53	55·62	55·72	55·82	55·91
1·46	56·01	56·11	56·20	56·30	56·39	56·49	56·59	56·68	56·78	56·87
1·47	56·97	57·06	57·16	57·25	57·35	57·44	57·54	57·63	57·73	57·82
1·48	57·92	58·01	58·10	58·20	58·29	58·38	58·48	58·57	58·66	58·75
1·49	58·85	58·94	59·03	59·12	59·22	59·31	59·41	59·50	59·59	59·68
1·50	59·78	59·87	59·96	60·05	60·14	60·23	60·33	60·42	60·51	60·60
1·51	60·69	60·78	60·87	60·96	61·05	61·14	61·24	61·33	6..42	61·51
1·52	61·60	61·69	61·78	61·87	61·96	62·05	62·14	62·23	62·32	62·41
1·53	62·50	62·59	62·68	62·77	62·86	62·95	63·04	63·13	63·22	63·31
1·54	63·40	63·49	63·58	63·67	63·76	63·85	63·94	64·03	64·12	64·20
1·55	64·29	64·38	64·47	64·55	64·64	64·73	64·82	64·91	65·00	65·08
1·56	65·17	65·26	65·35	65·44	65·52	65·61	65·70	65·79	65·88	65·96
1·57	66·05	66·14	66·23	66·31	66·40	66·49	66·57	66·66	66·75	66·83
1·58	66·92	67·01	67·10	67·18	67·27	67·36	67·44	67·53	67·62	67·70
1·59	67·79	67·88	67·97	68·05	68·14	68·23	68·31	68·40	68·49	68·57
1·60	68·66	68·74	68·83	68·92	69·00	69·09	69·17	69·26	69·35	69·43
1·61	69·52	69·60	69·69	69·78	69·86	69·95	70·03	70·12	70·20	70·29
1·62	70·38	70·46	70·55	70·63	70·72	70·80	70·89	70·97	71·06	71·14
1·63	71·23	71·31	71·40	71·48	71·57	71·65	71·74	71·82	71·91	71·99
1·64	72·07	72·16	72·25	72·33	72·42	72·50	72·59	72·67	72·76	72·84
1·65	72·93	73·01	73·10	73·18	73·27	73·35	73·43	73·52	73·60	73·69
1·66	73·77	73·86	73·94	74·02	74·11	74·19	74·27	74·36	74·44	74·53
1·67	74·61	74·69	74·78	74·86	74·95	75·03	75·12	75·20	75·29	75·37
1·68	75·46	75·54	75·63	75·71	75·80	75·88	75·97	76·05	76·14	76·22
1·69	76·31	76·39	76·48	76·56	76·65	76·74	76·82	76·91	76·99	77·08
1·70	77·17	77·25	77·34	77·42	77·51	77·60	77·68	77·77	77·85	77·94
1·71	78·03	78·11	78·20	78·28	78·37	78·46	78·54	78·63	78·72	78·80
1·72	78·89	78·97	79·06	79.15	79·23	79·32	79·41	79·49	79·58	79·67
1·73	79·75	79.84	79·93	80·02	80·11	80·20	80·29	80·38	80·47	80·56
1·74	80·65	80·74	80·83	80·92	81·01	81·10	81·19	81·28	81·37	81·46
1·75	81·55	81·64	81·73	81·82	81·92	82·01	82·11	82·21	82·31	82·41
1·76	82·51	82·61	82·71	82·80	82·90	83·00	83·10	83·20	83·29	83·39
1·77	83·49	83·59	83·69	83·78	83·88	83·98	84·08	84·18	84·29	84·39
1·78	84·50	84·60	84·71	84·81	84·92	85·03	85·14	85·25	85·36	85·47
1·79	85·60	85·72	85·84	85·96	86·08	86·20	86·32	86·45	86·58	86·71
1·80	86·84	86·97	87·10	87·23	87·36	87·50	87·64	87·78	87·92	88·06
1·81	88·20	88·34	88·49	88·64	88·79	88·95	89·11	89·27	89·44	89·61
1·82	89·79	89·97	90·15	90·33	90·51	90·70	90·90	91·10	91·30	91·52
1·83	91·74	91·98	92·22	92·46	92·71	92·98	93·26	93·56	93·87	94·20
1·84	94·57	94·96	95·40	96·02	96·93					
1·84	99·88	99·61	99·29	98·84	98·08					
1·8442	97·50									
1·8394	100·00									

For concentrated acid the determination of the specific gravity is not of

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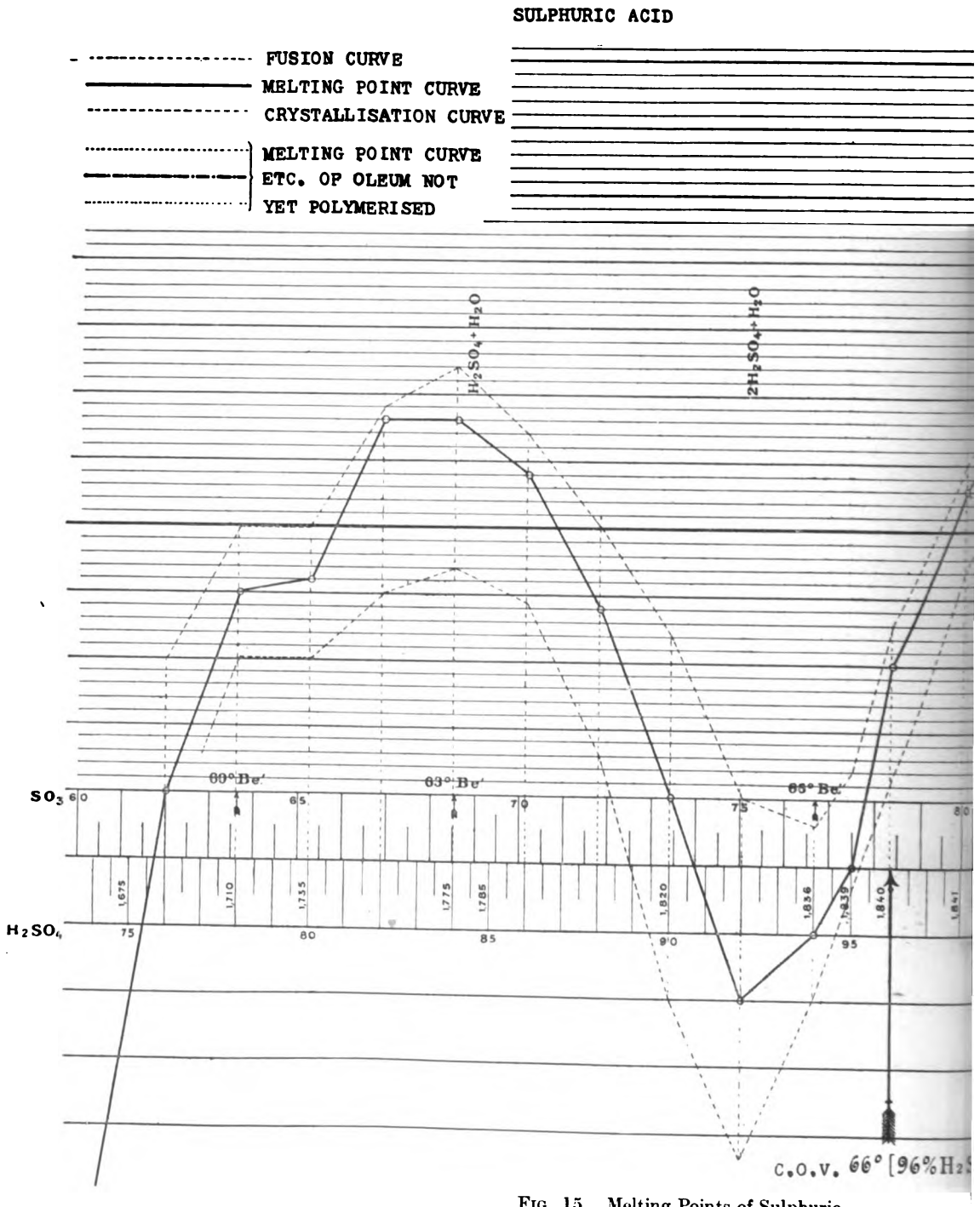

FIG. 15. Melting-Points of Sulphuric

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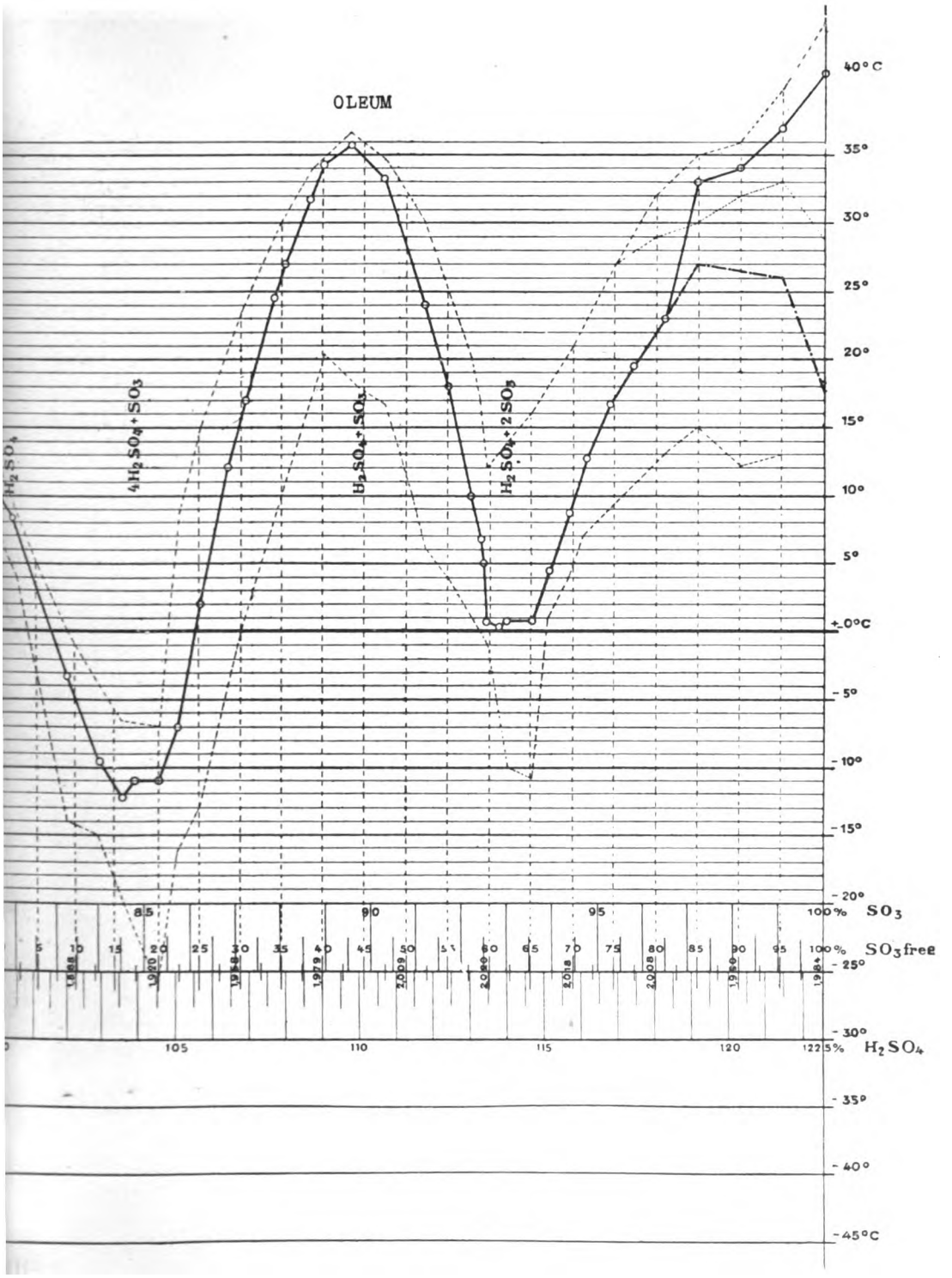

Acid and Oleum (Knietsch)

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much value as an indication of its strength because the density reaches a maximum at about 97·5 per cent.

The following Table gives the corrections to be applied to the specific gravities if the temperature varies from 15°.[1]

Sp. Gr.		Correction for 1°
Up to 1·170	....	0·0006
1·170 ,, 1·450	....	0·0007
1·450 ,, 1·580	....	0·0008
1·580 ,, 1·750	....	0·0009
1·750 ,, 1·820	....	0·0010

For the effect of impurities on the specific gravity of sulphuric acid *see* Marshall, *J.S.C.I.*, 1902, p. 1508. Fig. 16 gives the specific gravities of a

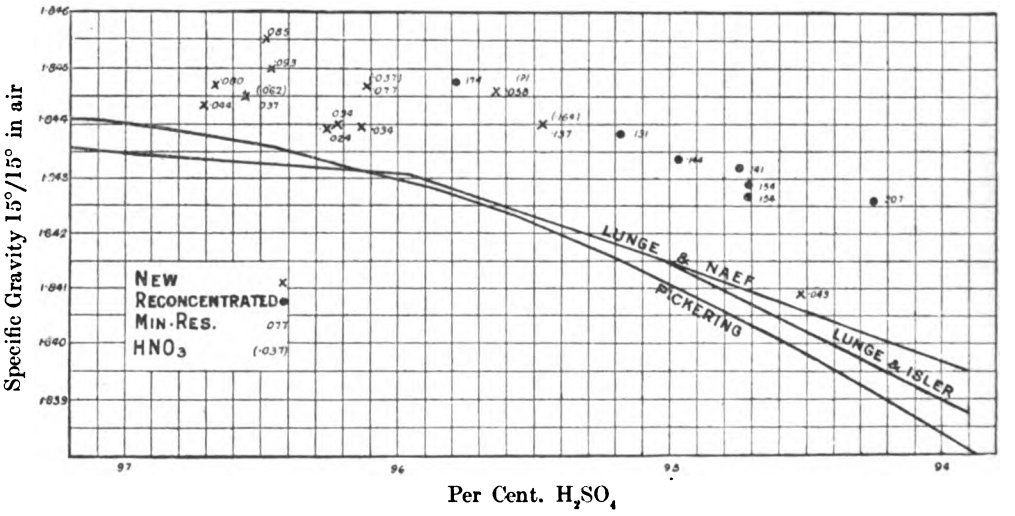

FIG. 16. Specific Gravities of Sulphuric Acid

number of trade samples of C.O.V., some of which had become contaminated with traces of nitric acid, also some acids that had been used and reconcentrated several times in a Kessler plant. The curves corresponding to the Tables of Pickering and Lunge are also given for comparison.

Knietsch has determined the specific gravities of fuming acids (*loc. cit.*). His figures are to be found in the Table on the next page.

Calculations. The strength of the fuming acid is generally expressed as per cent. free SO_3, but sometimes as total SO_3. When determining the strength by analysis it is most convenient to express it first as per cent. H_2SO_4, and there are other advantages in expressing it thus. A figure is, of course, obtained which is

[1] Lunge and Hurter, *Alkali-Maker's Pocket-book.*

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greater than 100, but it gives at once the quantity of sulphuric acid that will be formed if 100 parts of it be added to a mixture, and if 100 be deducted from it, the remainder is the amount of water that will disappear from the mixture to form this sulphuric acid. This remainder multiplied by SO_3/H_2O (= 80/18 = 4·44) gives the percentage of free SO_3. The percentage of H_2SO_4 multiplied by 80/98 (= 0·8163) gives the total SO_3. Similar rules may be made for converting any of these three expressions into any other :

if	F	be the percentage of free SO_3
and	T	,, total SO_3
and	H	,, H_2SO_4
then	F	= 4·444 (H − 100)
		= 5·444 T − 444
and	T	= 0·8163 H
		= 0·1837 F + 81·63
and	H	= 0·225 F + 100
		= 1·225 T

The conversion can also be effected by means of the scales at the base of Fig. 15.

Free SO_3 per cent.	Total SO_3	Corresponding H_2SO_4	Sp. gr. 15°/15° in air	Sp. gr. 45°
10	83·46	102·2	1·888	1·858
20	85·30	104·5	1·920	1·887
30	87·14	106·7	1·957	1·920
40	88·97	109·0	1·979	1·945
50	90·81	111·2	2·009	1·964 (max.)
60	92·65	113·5	2.020(max.)	1·959
70	94·48	115·7	2.018	1·942
80	96·32	118·0	2·008	1·890
90	98·16	120·2	1·990	1·864
100	100·00	122·5	1·984	1·814

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CHAPTER VIII

NITRIC ACID

Manufacture : Recovery of nitrous fumes : Storage : The distillation : Nitric acid from the atmosphere : Properties : Specific gravities : Freezing-points : Boiling-points : Vapour pressures

Manufacture. NITRIC acid is usually made by distilling Chili saltpetre with sulphuric acid in large iron retorts. Formerly these were made of such a size as to take a charge of about half a ton of sulphuric acid and the same quantity of nitrate : now they are generally made to take twice as much or more. Fig. 17 shows a retort somewhat similar to those used for the Valentiner system. To take a ton of nitrate the retort should be about 6 feet in diameter and 6 feet high : it must not be too small on account of the danger of frothing over or " priming."

Condensers. The nitric-acid vapours were formerly condensed by air cooling, by leading them through a large number of stone-ware jars connected by stone-ware pipes, but this system was inefficient and required much plant and space. The reason for its adoption was that metal condensers could not be used because they were attacked by the acid, and stone-ware condensers cooled with water would have cracked with the changes of temperature. But with the improvements that were made in the manufacture of earthen and stone-ware this has been altered. The Guttmann condensing battery has been much used (Fig. 18). It consists of a number of vertical stone-ware pipes immersed in a tank through which water circulates ; at the bottom these pipes are connected by cross-pieces in such a way that whilst the fumes have to pass up and down the pipes one after the other, the condensed acid flows along from one cross-piece to another through inverted siphons and finally to the storage tank.

In the Valentiner plant (Fig. 19) stone-ware coils are used, and these are also adopted now by many who do not work by Valentiner's system. When first introduced there were frequent breakages, especially at the upper extremity where the coil entered the water. The coils could be repaired by the addition of a piece of lead pipe joined on, for the strong acid has but little action upon it. Such breakages are not so frequent now : they can be avoided to a large extent by not immersing the first coil in water, but cooling it by running water over cloths laid on the coil. Coils can now be obtained made of fused

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silica or " vitreosil " as much as 2 inches in diameter and 60 feet long. These are much more resistant than stone-ware and can be repaired when broken.

The principal peculiarity of Dr. Valentiner's system is that the distillation is carried out *in vacuo*. At the end of the series of condensers and jars shown in Fig. 19 there is a vacuum pump, which with every stroke draws in some

Valentiner system.

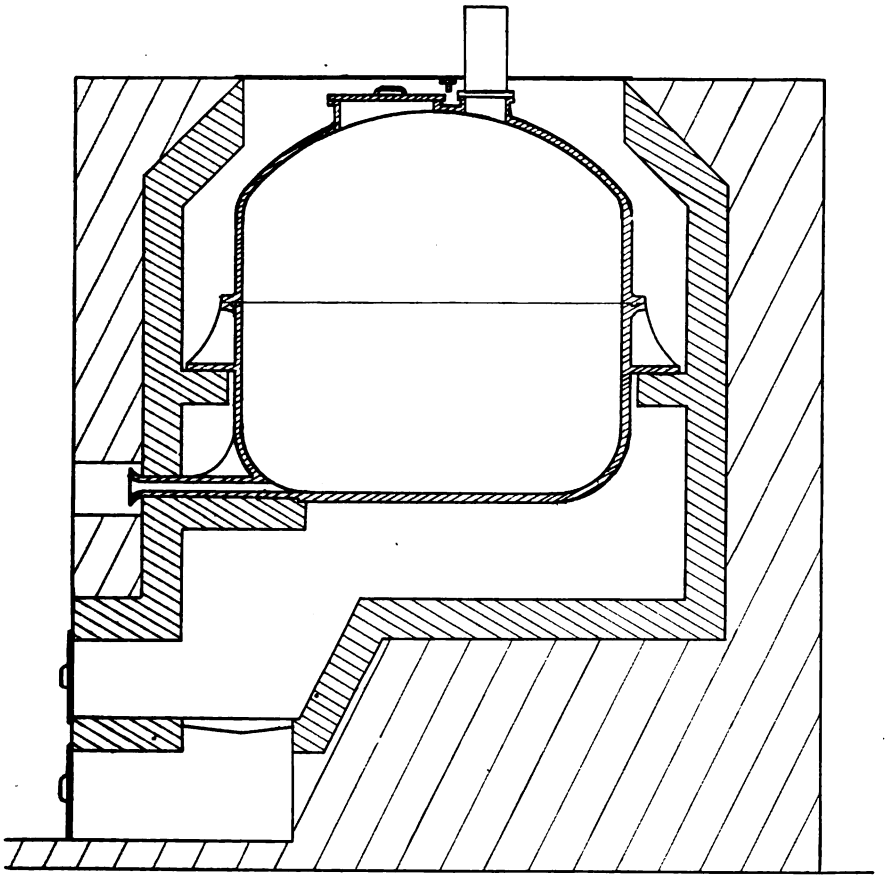

FIG. 17. Nitric Acid Still

caustic soda solution to prevent the acid fumes attacking the metal of the pump too much. The large number of small washing jars is also to absorb the acid fumes as far as possible before they reach the pump. The advantages claimed for the system are that the time of working a charge is much shortened by the use of a vacuum, that the process is under better control, and that there is less breakage of coils because the temperature is lower, also that the acids are purer. The plant is well designed and made, and consequently

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the users have generally found it satisfactory, but some who have tried working both with and without vacuum state that they can achieve equally good results at the ordinary pressure, and with less complicated appliances.

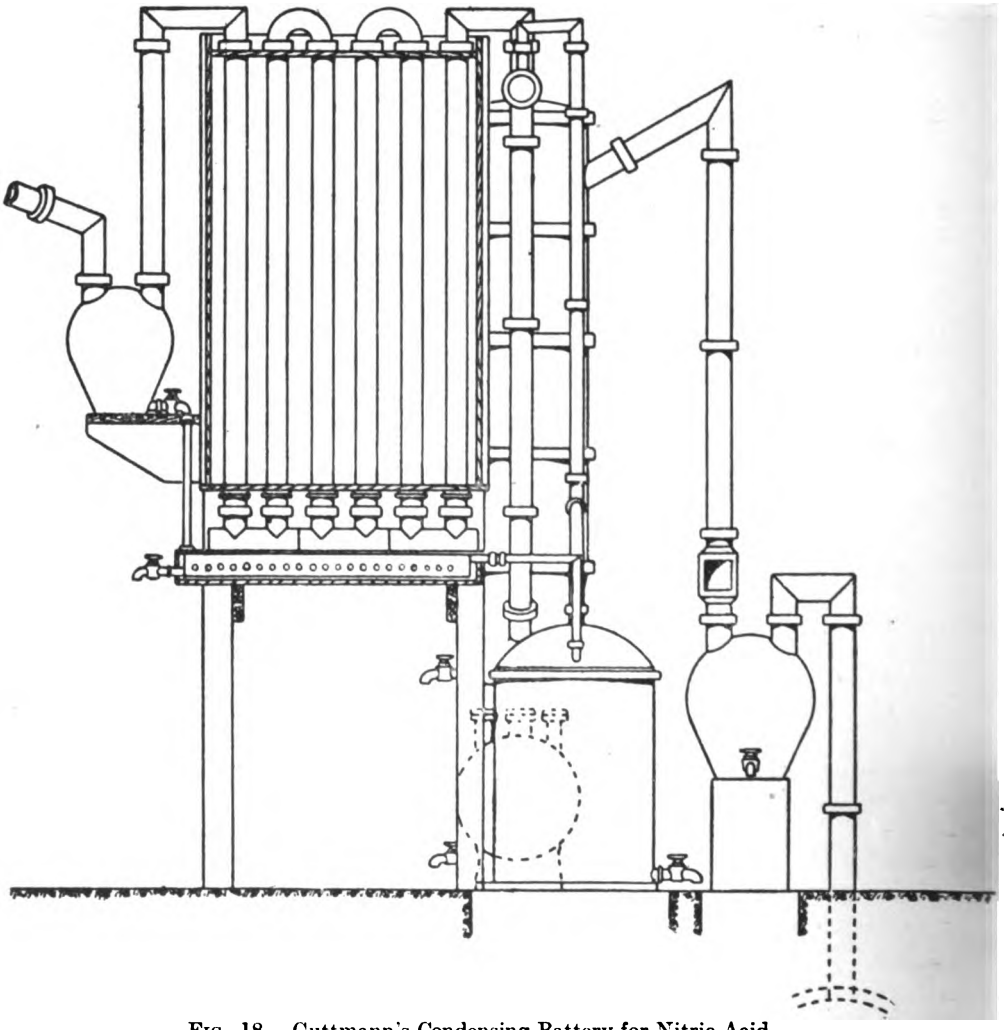

FIG. 18. Guttmann's Condensing Battery for Nitric Acid

Recovery of nitrous fumes.

In the retort a certain proportion of the nitric acid is always reduced through various causes to lower oxides of nitrogen. Some of this is dissolved by the strong acid in the condensers and is an objectionable impurity. In order to prevent this solution taking place air is sometimes drawn over the acid whilst it is still warm, and this carries away the greater part of the lower

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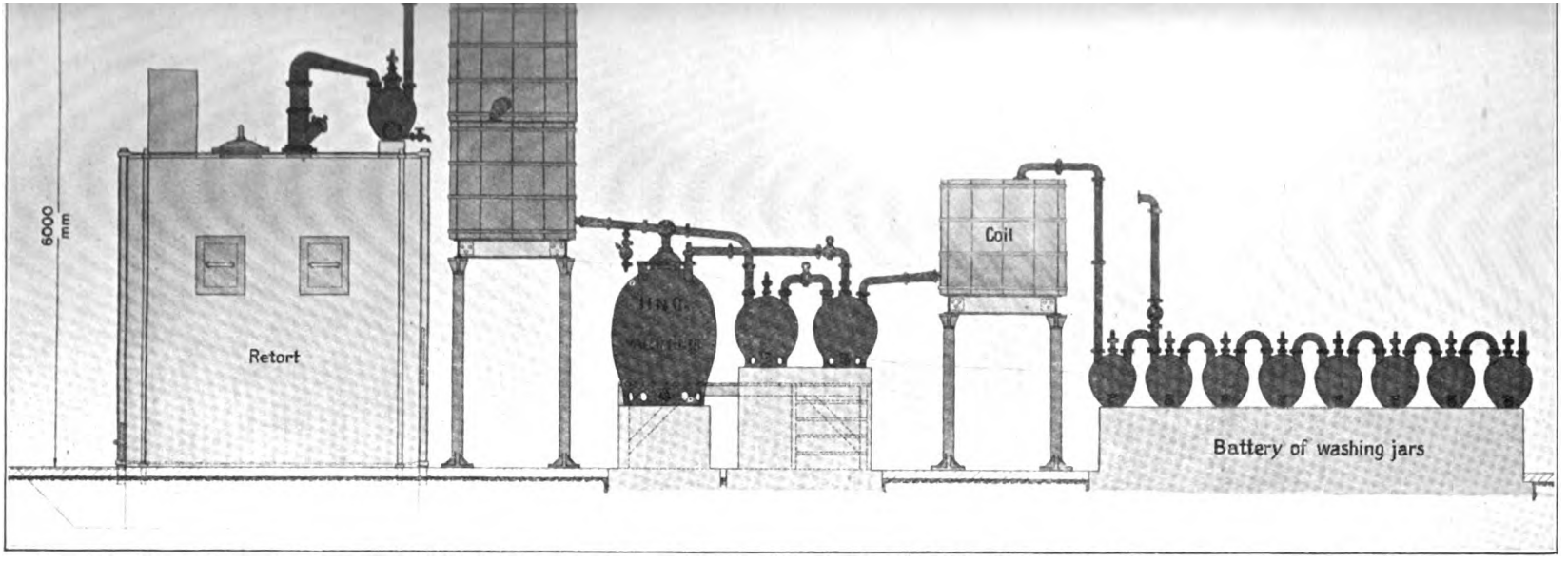

FIG. 19*a*. Valentiner's Nitric Acid Plant. Elevation

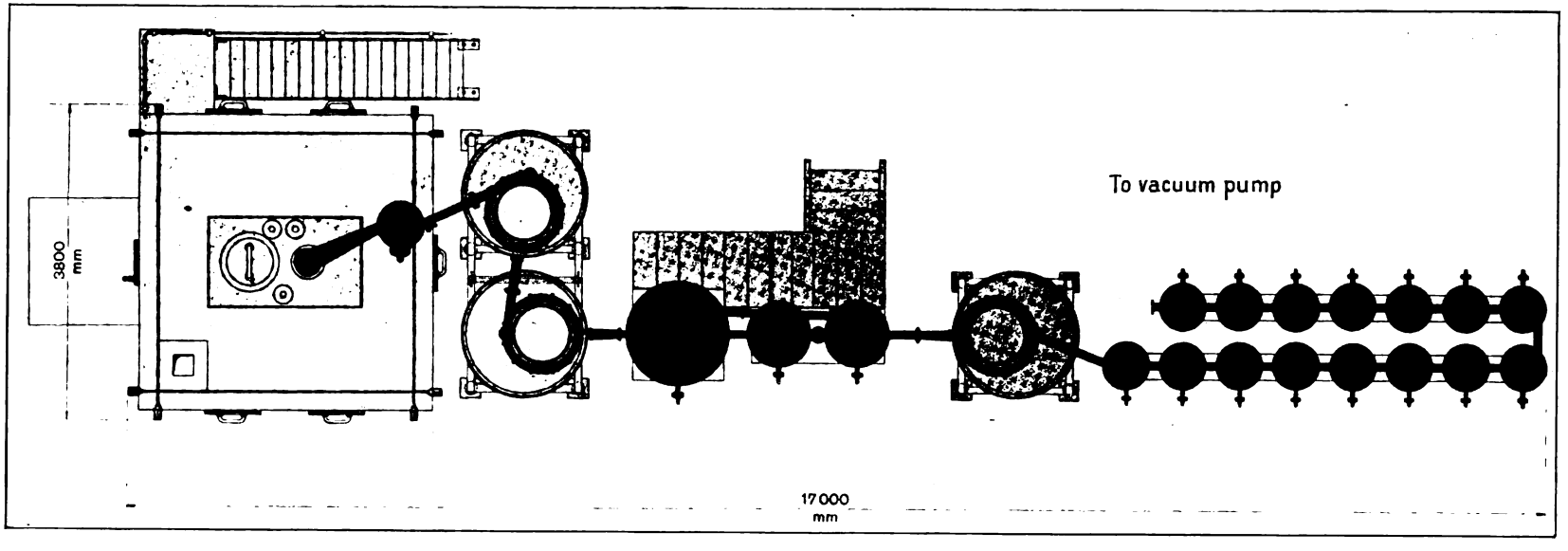

FIG. 19*b*. Valentiner's Nitric Acid Plant. Plan

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oxides. Whether this is done or not, there is always some nitrous gas that is not condensed in the coils, and this must be recovered not only because it is valuable, but also because it would cause a nuisance. After passing through the condensing coils, therefore, the residual gases are made to pass up a series of towers filled with Lunge-Rohrmann plates or Guttmann-Rohrmann balls. A jet of air is also introduced partly to draw the gases along better and partly to oxidize the nitrous gases. These consist principally of nitric oxide and nitric peroxide, NO and NO_2; the former is rapidly converted by free oxygen into the latter, so that then there is only NO_2, which when it comes in contact with water forms a mixture of nitric and nitrous acids:

$$2NO_2 + H_2O = HNO_3 + HNO_2$$

But nitrous acid is only sparingly soluble in water or weak nitric acid, and consequently it is given off again as a mixture of nitric oxide and peroxide:

$$2HNO_2 = NO + NO_2 + H_2O.$$

In the presence of oxygen and water the cycle of changes then recommences. Although the combination of the nitric oxide with oxygen is rapid, the reaction with water is rather slow, and consequently a considerable amount of tower space is necessary for the almost complete absorption of the fumes.

Storage of nitric acid. Nitric acid of 90 to 95 per cent. strength can be stored either in large stone-ware vessels or in iron tanks lined with chemical lead. The action of the acid on the lead is very slight, and such tanks last for years before they require to be relined. For weaker acid, stone-ware and glass are practically the only materials that are available. The maximum theoretical strength of acids running from a tower of this kind is that of the constant boiling mixture of nitric acid and water, which contains 68 per cent. of the former and has a specific gravity of 1·41 (42° B), but generally it is considerably weaker than this and has a specific gravity of about 1·38, corresponding to 61 per cent. HNO_3. If a series of towers is installed, the weak acid from one should be raised continuously and made to flow down the next in the opposite direction to that of the gases.

The distillation. The nitrate is dried by being spread on iron plates on the top of a retort, whilst a previous charge is being worked. It is passed in through the man-hole in the top of the retort, sulphuric acid is run in, and the lid of the man-hole is closed and luted down with clay or a mixture of asbestos powder and water-glass. Theoretically, 1·153 parts of H_2SO_4 are required to convert 1 part of $NaNO_3$ into $NaHSO_4$: in practice it is usual to add rather less, 1·04 to 1·08 parts so that a small proportion of the neutral sulphate Na_2SO_4 is formed. To use too much acid would not only involve a waste

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of this substance, but would make the bisulphate too soft and acid, and therefore difficult to handle. It is always well to add a little weak nitric acid to the charge or some weaker sulphuric acid. In this way not only is some of the weak acid worked up, but the yield of good nitric acid is increased. If the charge is practically free from water, some of the nitric acid in the retort is converted into nitric anhydride, which breaks down very readily into nitric peroxide and oxygen, and produces a dark acid. The charge having been introduced, the fire is lit and the retort is gradually heated. If working *in vacuo* under a pressure of 7 inches of mercury, acid begins to come over at about 100° C.; if at atmospheric pressure, somewhat higher. As the distillation becomes more active, the heat must be moderated to prevent priming. The first runnings are liable to contain a considerable proportion of hydrochloric acid and other impurities as well as much nitrous acid. Therefore, if acid of good quality be required the first portion should be collected separately and not added to the main bulk, or a current of air should be drawn over the still warm acid as mentioned above. The last runnings are liable to be rather weak, so that if acid of the highest strength be required they also should be collected separately.

When the charge is finished, and whilst the contents of the retort are still hot, the plug in the opening at the bottom is removed, and the residue in the retort is allowed to run out through a removable gutter into a trolley or a shallow cast-iron trough. The latter is preferable, as the "nitre-cake" is easier to break up if it is in a thin layer. This is done by means of a crowbar or sledge-hammer, and the broken cake is removed to a convenient place of storage until it can be disposed of. The nitre-cake is generally used either for making superphosphate manure or hydrochloric acid and sodium sulphate; in out-of-the-way districts its disposal is often a matter of some difficulty, as its value is small, and it is troublesome to transport on account of its corrosive properties. Nitre-cake consists mostly of sodium bisulphate with some neutral sulphate, a fair amount of moisture (especially if it has been exposed to the atmosphere long or has been rained on), a little nitric acid, and other impurities.

To work off a charge of nitric acid takes about ten hours, but it is claimed that in the latest Valentiner plant it can be done in four and a half hours.

Nitric acid from the atmosphere.

There are now large installations in Norway and elsewhere in which the oxygen and nitrogen are made to combine with one another under the influence of an electric discharge or otherwise. The oxide of nitrogen is then made to combine with water and more oxygen to form weak nitric acid, much in the way described above. The acid so produced is too weak to use in the manufacture of explosives without first concentrating it, and liquid nitric acid is troublesome to transport. Nitric acid from this source has not therefore been used much for the manufacture of explosives.

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Properties of nitric acid.

The concentrated acid has very little action upon metals. The more dilute acid acts energetically on all the common metals; if the acid be quite free from nitrous acid there is no action, but as commercial acid always contains some nitrous this is not a matter of great practical importance.

Specific gravities.

The Tables of Lunge and Rey superseded the earlier inaccurate ones, but the more recent determinations of Veley and Manley [1] are more numerous. The figures have been interpolated graphically, those above 63 per cent. by Veley and Manley, those below by myself, and are given in the following Table:

SPECIFIC GRAVITIES OF NITRIC ACID AT 15°/4° IN VACUO

(Veley and Manley)

Specific gravity	Per cent. HNO_3	Difference for 1° C.	Specific gravity	Per cent. HNO_3	Difference for 1° C.
1·000	0·02	·0001	1·270	42·7	·0010
1·010	1·90	·0002	1·280	44·3	·0011
1·020	3·8	·0002	1·290	45·8	·0011
1·030	5·6	·0002	1·300	47·4	·0011
1·040	7·3	·0003	1·310	49·0	·0011
1·050	9·0	·0003	1·320	50·5	·0012
1·060	10·7	·0004	1·330	52·1	·0012
1·070	12·4	·0004	1·340	53·8	·0012
1·080	14·0	·0005	1·350	55·6	·0013
1·090	15·6	·0005	1·360	57·6	·0013
1·100	17·2	·0005	1·370	59·5	·0013
1·110	18·9	·0005	1·380	61·4	·0014
1·120	20·5	·0006	1·390	63·1	·0014
1·130	22·0	·0006	1·400	65·1	·0014
1·140	23·5	·0006	1·410	67·4	·0016
1·150	25·0	·0007	1·420	69·6	·0015
1·160	26·5	·0007	1·430	72·0	·0015
1·170	28·0	·0007	1·440	74·5	·0015
1·180	29·5	·0007	1·450	77·0	·0016
1·190	31·0	·0008	1·460	80·3	·0016
1·200	32·4	·0009	1·470	83·3	·0016
1·210	33·8	·0009	1·480	86·3	·0017
1·220	35·3	·0010	1·490	89·6	·0017
1·230	36·8	·0010	1·500	94·0	·0017
1·240	38·2	·0010	1·510	97·8	·0018
1·250	39·6	·0010	1·520	99·8	·0020
1·260	41·1	·0010			

The influence of nitric peroxide on the specific gravity is considerable

[1] *Phil. Trans. A.*, vol., 191, p. 365 (1898), and *Proc. Roy. Soc.*, 1901, p. 86, and *J.S.C.I.*, 1903, p. 1227.

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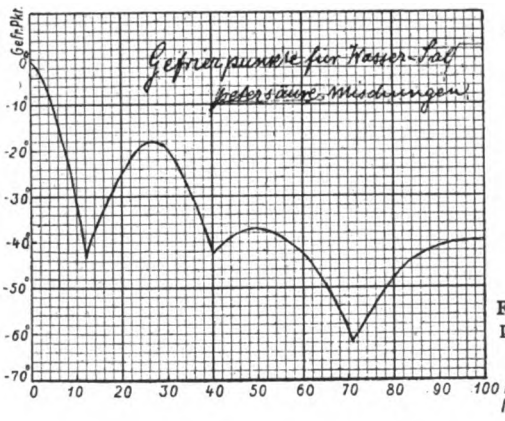
and has been ascertained by Lunge and Marchlewski [1] for an acid having the specific gravity 1·496.

Per cent. N_2O_4	Alteration of sp. gr.	Per cent. N_2O_4	Alteration of sp. gr.
0·25	·0005	5·0	·0323
0·50	·0008	6·0	·0395
0·75	·0015	7·0	·0465
1·00	·0030	8·0	·0533
1·25	·0048	9·0	·0600
1·50	·0068	10·0	·0660
1·75	·0078	11·0	·0730
2·00	·0105	12·0	·0785
3·0	·0180	12·75	·0835
4·0	·0253		

The figure in the second column is to be subtracted from the specific gravity before ascertaining the strength of the nitric acid by means of the specific gravity Table. The amount of lower oxide is, however, often calculated as nitrous acid. The figures in the first column of the above Table must be multiplied by ·519 to give the corresponding amounts of nitrous acid in accordance with the equation :

$$N_2O_4 + H_2O = HNO_2 + HNO_3.$$



Freezing-points.

FIG. 20. Freezing-points of Nitric Acid

The freezing-points of mixtures of nitric acid and water are shown in Fig. 20, which is based on the determinations of Küster and Kremann.[2] It will be seen that all mixtures solidify at temperatures considerably below the freezing-point of water. In the first portion of the curve ice separates out, in the second crystals of $HNO_3,3H_2O$, in the third HNO_3,H_2O, and in the last solid nitric acid.

Pure nitric acid boils at about 86° C. under atmospheric pressure, and at 21·5° under a pressure of 24 mm. When water is added to the acid the boiling-point increases until it reaches a maximum at about 68 per cent. HNO_3, and then falls again. If acid either stronger or weaker than this be evaporated

Boiling-points.

[1] *Ang.*, 1892, p. 10.

[2] *Z. f. anorg. C.*, 1904, p. 21.

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or fractionally distilled, the composition tends to approach this percentage, and when it is reached the mixture distils unchanged. The composition of the constant boiling mixture depends upon the pressure, however; *in vacuo* a mixture containing 66·3 molecular per cent. HNO_3 boils at 13°, giving a distillate of the same composition; under 735 mm. pressure the constant boiling mixture contains 62·2 molecular per cent. and boils at 120·5°; under 1220 mm. the composition is 61·6 molecular per cent.[1]

Vapour pressures.

Saposhnikoff has made a few determinations of the vapour pressures of nitric acid at 15° C.[2]

Per cent. HNO_3	Vap. pres. 15° C. mm.	Per cent. N in vapour	Molecular per cent. HNO_3
98·0	46·2	23·7	93·5
92·9	42·6	23·5	79·0
88·6	29·7	23·0	68·7
82·1	16·6	22·6	56·5
78·1	9·4	22·5	50·0
65·3	1·9	19·3	34·7

With reference to the third column of the above Table it is to be borne in mind that HNO_3 contains 22·2 per cent. N. It is therefore evident that the vapours from the nitric acid contain nitric peroxide or nitric anhydride, which have 30·6 and 25·9 per cent. N respectively.

[1] Roscoe, *Lieb. An.*, 1860, pp. 116, 203.

[2] *Z. phys. C.*, 1905, pp. 53, 225.

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CHAPTER IX

MIXED AND WASTE ACIDS. MANIPULATION

Mixed acid : Mixing the acids : Properties of mixed acids : Specific gravities : Vapour pressures : Waste acid : Gun-cotton waste acid : Nitro-glycerine waste acid : Denitration plant : Manipulation of acids : Materials : Eggs : Oleum

NITRATION, whether of glycerine or cotton or an aromatic compound, such as toluene, is always carried out with a mixture of sulphuric and nitric acids, and not with nitric acid alone, for even the strongest nitric acid does not act well by itself. One of the main functions of the sulphuric acid is to combine with the water that is formed during the reaction and prevent it diluting the nitric acid, but it appears probable that it also takes an active part in the reaction, and that to some extent at any rate it combines first with the substance to be nitrated to form a sulphuric ester or sulphonic acid, and that it is this which is afterwards acted upon by the nitric acid.

Mixing the acids.

The two acids are mixed together in iron tanks. For work on a moderately large scale old steam-boilers can be used for this purpose, the fire tubes being removed and the openings closed by riveting on plates. For work on a large scale it is better to have special tanks built, large enough to hold several days' supply of mixed acid. The best form is a cylinder with its axis vertical, the height being somewhat less than the diameter. Passing through the cover there should be a shaft to which arms are attached, so that by rotating the shaft the contents of the tank can be stirred. When the mixing is carried out in small boilers the agitation of the liquid usually has to be effected by blowing air through it, which causes a slight loss of nitric acid.

Properties of mixed acids.

When nitric acid is added in small quantities to sulphuric acid, the specific gravity at first rises sharply in spite of the fact that nitric acid has a lower density than sulphuric. The specific gravity attains a maximum and then falls again, as is shown in Fig. 21 and in the Table [1] on p. 102. Saposhnikoff [2] has obtained similar results. The following are two maximum specific gravities observed by him with mixtures containing different amounts of water :

Sp. gr. 25°/25°	1·8810	1·8615
Sulphuric acid	89·32 per cent.	89·94 per cent.
Nitric acid	10·13 „	6.57 „
Water	·28 „	3·49 „
Oxide of nitrogen	·27 „	— „

[1] Marshall, *J.S.C.I.*, 1902, p. 1508. [2] *Z. f. physik. C.*, 1904, pp. 49, 697 ; 1905, pp. 53, 225.

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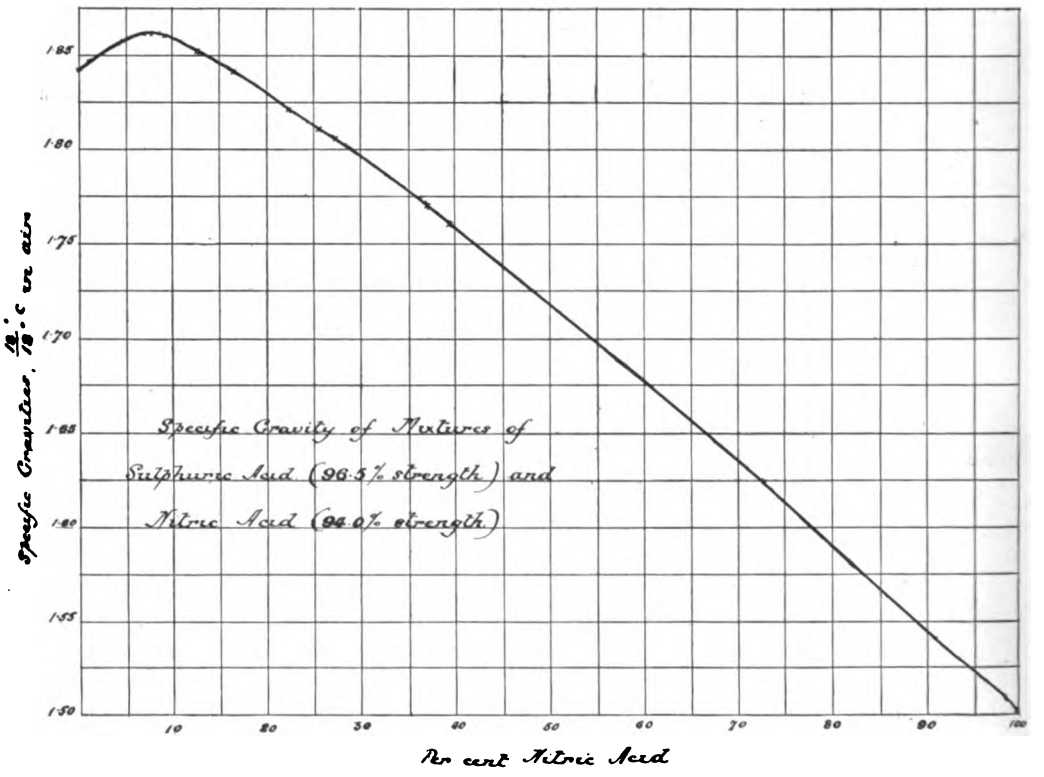

FIG. 21. Specific Gravities of Mixed Acids (Marshall)

HNO_3	Sp. gr. 18°/18° in air	HNO_3	Sp. gr. 18°/18° in air
Per cent.		Per cent.	
0·00	1·8437	22·51	1·8215
0·57	1·8456	25·56	1·8112
1·05	1·8476	27·29	1·8053
4·67	1·8586	32.53	1·7863
7·17	1·8618	37·03	1·7700
7·37	1·8620	39·49	1·7601
7·75	1·8619	57·78	1·6879
9·10	1·8605	72·89	1·6227
11·33	1·8557	90·76	1·5408
12·71	1·8520	98·19	1·5080
16·52	1·8414	100·00	1·5009

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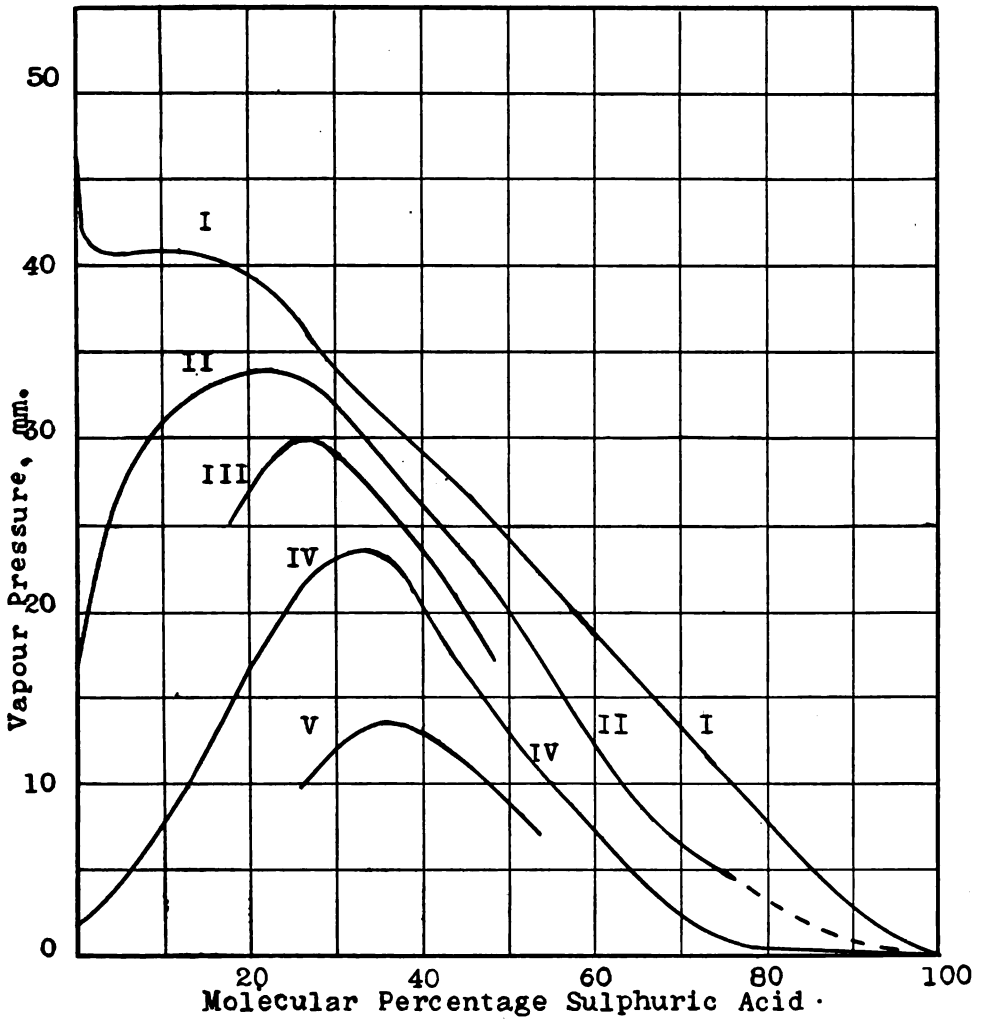

FIG. 22. Vapour Pressures of Mixtures of Sulphuric Acid with Nitric Acids of Various Strengths

Curve	Strength of nitric acid, per cent. By weight	Molecular
I.	98·0	93·5
II.	85·2	62·3
III.	77·8	50·0
IV.	65·5	35·4
V.	50·0	22·2

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The second of the above is almost identical both in composition and density with the maximum observed by Marshall. From the results of his measurements of the vapour pressures Saposhnikoff came to the conclusion that there is little or no combination of the two acids to form complex molecules, and he ascribed these high specific gravities to the formation of nitric anhydride, N_2O_5. But as this substance has a specific gravity of only 1·64, the explanation does not appear sufficient. It seems possible that the high densities are due to some reversible reaction taking place between the sulphuric and nitric acids.

Vapour pressures.

Saposhnikoff's determinations of the vapour pressures of mixed acids are shown in the curves in Fig. 22, in which mm. of pressure are plotted against the molecular percentage of sulphuric acid in the mixtures. The sudden fall at the left end of curve *I* is due to the fact that the nitric acid used contained about 0·9 per cent. of nitric oxide, which is very volatile as compared with nitric acid. When a little sulphuric acid was added it combined with this to form nitro-sulphuric acid, which is not volatile. Through the greater part of its course this curve is practically straight: if the acids had been quite anhydrous and free from impurities it would probably have been straighter. With acids containing water the addition of sulphuric acid increases the vapour pressure, because it combines with the water and decomposes the compound of nitric acid and water. The pressure is at a maximum when there is nearly a molecule of sulphuric acid for each one of water: then it falls again. These vapour-pressure curves are also given in another form in Fig. 26, which shows the connexion between the vapour pressure and the degree of nitration of cotton. That there should be such a connexion might have been anticipated, as the activity of a substance in solution generally increases when the vapour tension increases, but mixtures with equal vapour pressures do not by any means always produce nitro-cottons with equal amounts of nitrogen, as a careful examination of the diagram will show.

WASTE ACID

Gun-cotton waste acid.

The waste acid from the manufacture of nitro-cotton is usually revivified by the addition of strong sulphuric and nitric acid, and used again, but if the whole quantity were strengthened up in this way each time the quantity would steadily increase. It is therefore necessary to discard some of the waste acid. The quantity of waste acid produced in the displacement process for the manufacture of gun-cotton is more than in the older methods, for the recovery of the waste acid is much more complete and some of it becomes diluted with the water used for the displacement. When nitrated by the Abel process or in centrifugals a considerable amount of acid remains in the gun-cotton after the bulk has been removed in the centrifugals. If oleum of 60 to

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70 per cent. be used together with nitric acid of about 93 per cent. strength, the fresh acid does not bring the volume of acid much above its original bulk, for it does not much exceed what is lost in the manner just mentioned, together with the nitric acid actually consumed in the nitration. In small factories, which do not possess the plant for working up the waste acids again, this is a great advantage because only a very inadequate price can be obtained for the waste acid if it has to be sold. Where the nitric acid can be recovered on the spot it is more usual to use oleum of 20 to 25 per cent. strength.

These revivified acids are little, if at all, less efficient than new acid, at any rate for the manufacture of the more insoluble varieties of nitro-cellulose. The organic impurities formed in the nitration process apparently either pass away in the nitrated product and so eventually into the waters used for the purification, or else are oxidized completely away by the acid if they have passed into solution. The quantity of organic impurity in the acids remains small therefore; but Will found nitro-sugars in the acids.

The portion of the waste acid that is not revivified can generally be utilized to some extent for the manufacture of nitric acid. The remainder, if any, must be reconverted into the separate acids, nitric and sulphuric. The greater part of the nitric acid can be distilled off in a retort, and is thus obtained as concentrated acid again. Some weak nitric acid can be added to the charge in the retort at the same time, and so be worked up again. It is not practicable to distil off the last traces of nitric acid in this way, and consequently it is necessary to pass the residual sulphuric acid down the denitrating tower before reconcentrating it in a Kessler plant. In many works no attempt is made, however, to recover any of the nitric acid in concentrated form, and all the waste acid to be treated is passed at once down the denitrating tower.

Nitro-glycerine waste acid.

The waste acid from the manufacture of nitro-glycerine always contains some of this substance, or mono- or di-nitro-glycerine in solution. When the waste acid is heated this decomposes with the production of considerable quantities of the lower oxides of nitrogen. For this reason it is difficult to obtain strong nitric acid of good quality directly from it. It cannot be revivified either, because the organic matter in solution would be liable to decompose when the acid was heated by the addition of strong sulphuric acid. Moreover, there would be some nitro-glycerine formed, which would separate out in the storage tanks and other places and give rise to accidents. The whole of the nitro-glycerine waste acid has therefore to be denitrated.

Denitration plant.

The denitration of the waste acid is carried out in a tower, down which the acid runs: at the bottom steam or hot air, or both, are blown in. The nitric and nitrous acids are thus removed from the liquid and pass up the tower as vapour and gas respectively. These towers are frequently made of volvic stone cemented together with water-glass and asbestos powder,

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and filled with pieces of broken stone-ware and glass. They are often as much as 10 feet high and 18 inches in diameter to deal with some 1500 lbs. of acid per hour, but a much smaller plant would deal with this quantity equally effectively, or if a large tower be used a far larger quantity of acid can be passed down it if it be properly designed. It is, of course, important that the liquid and gases be well distributed and brought into intimate and repeated contact with one another. In England it is usual to denitrate with steam only : it is thus easy to drive the nitric acid completely out of the weak sulphuric. This is facilitated by the dilution which the sulphuric acid undergoes from the condensation of the steam, for weak sulphuric acid does not retain nitric and nitrous acids so obstinately as when it is concentrated. In Germany the steam is often made to inject heated air with it into the base of the denitrating tower : [1] a somewhat stronger sulphuric acid is thus obtained, containing 78 instead of 70 per cent., but as it has to be reconcentrated in any case, this is not a matter of great practical importance. In Evers's patent plant steam and hot air are injected at four different places in the tower (*see* Fig. 23) ; the heat of the sulphuric acid flowing from the base of the tower is utilized to heat the air.

Recovery of nitric acid.

The gases escaping from the top of the tower consist of nitric acid, water vapour and oxides of nitrogen, and if air has been injected nitrogen and oxygen, also some carbon monoxide and dioxide from the decomposition of the organic matter in the waste acid. In order to condense the nitric acid it is necessary to cool the gases. Formerly this was done by air cooling, the gases being led through a number of earthenware jars or " tourils " ; in the Evers plant (Fig. 23) air-cooled earthenware pipes are used, the surface being increased by subdividing the pipes at intervals into a large number of small pipes. The best method of cooling is, however, to take the gases through pipes immersed in a trough of water so arranged that the condensate can flow away into receivers. Before cooling the gases they should be mixed with air, if it has not already been injected in sufficient quantity. This oxidizes any nitric oxide to peroxide, and if water be present it converts part of it into nitric acid.

From the condenser the gases pass to absorption towers, where they meet a stream of water and the remaining nitric oxide is converted into nitric acid. It is essential that an excess of oxygen be present in the gas to effect the conversion in accordance with the equation : $4NO_2 + O_2 + 2H_2O = 4HNO_3$. Whether the condensation is complete can be seen by the appearance of the gas escaping from the last tower : it should not be red nor give much fume with the air. Whether there is an excess of oxygen in the gases can be ascertained by analysis : a sample of the gas is first shaken with distilled water until there is no further absorption, then with caustic alkali to absorb

[1] *See* Rudeloff, *S.S.*, 1907, p. 257.

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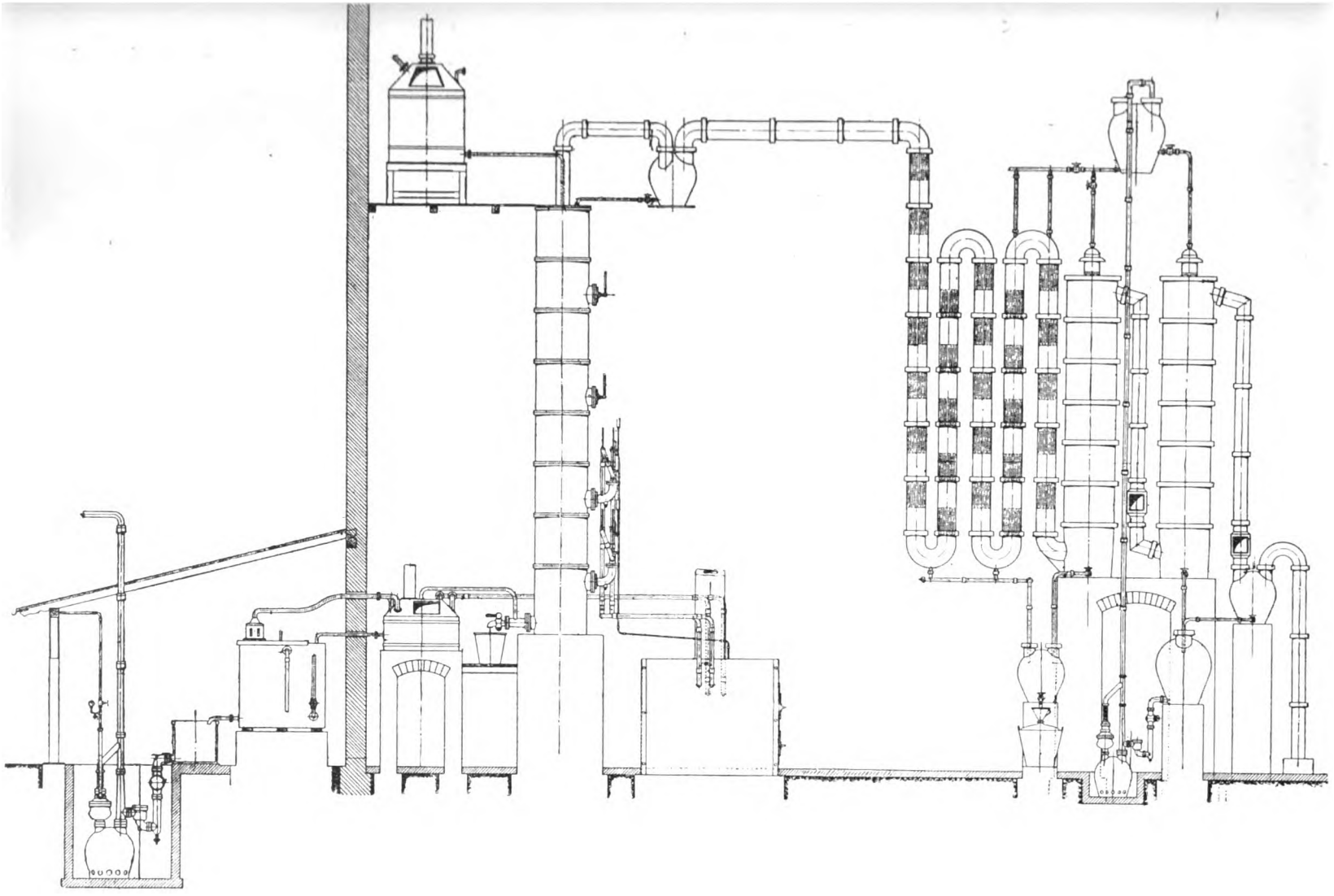

FIG. 23. Evers's Patent Denitrating Plant

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any carbon dioxide, and finally with alkaline pyrogallol, when there should be a distinct further diminution of volume.

The absorption towers are of stone-ware and should be filled with some acid-resisting material so as thoroughly to distribute both the ascending gas and the descending liquid, and bring them repeatedly into intimate contact with one another and cause them to mix. The Lunge plates do all this very efficiently if they are in perfect working order, but if the plates are not quite true, or if they get slightly out of the level, the liquid all runs down one side of the tower and the gas ascends on the other, and very little absorption takes place. If one lays one's hand on a Lunge tower that is working, one will often find that at one part of the circumference the shell is quite hot whilst the rest is cold, showing that action is only taking place in a portion of the tower. Guttmann's hollow stone-ware balls give a very good result and have the merit that no special care is required in filling them into the tower. There are many other forms of stone-ware filling for towers procurable. In order to effect complete absorption of the oxides of nitrogen two or three towers are necessary A slow stream of water is run into the last one and distributed uniformly over the cross-section of the tower. A weak nitric acid runs out at the bottom of the tower and is raised from there by means of a continuously acting appliance to the top of the next one. As weak nitric acid attacks all the common metals, glass and stone-ware are the only materials that can be used for the construction of the pipes and vessels. For raising the liquid to the tops of the towers small Kestner automatic eggs made of stone-ware can be used, but as the quantity is very small it is better to use a small appliance, which causes the acid to raise itself and works on the well-known principle of making the ascending column of liquid lighter than a descending one by mixing it with air. From the base of a tower a glass tube descends a distance equal to about half the height of the tower. It then turns through 180°, and a small distance beyond the bend compressed air is injected in through a number of small holes. When once the rate of admission of the air has been adjusted the appliance works continuously and requires very little attention. The mixture of acid and air should be delivered into the top of the tower below the cover, so that the air cannot carry away part of the acid fumes. This air also serves a useful purpose in that it renews the supply of oxygen, which has been partially exhausted by the oxidation of the nitrous gases. The greater part of the absorption of the gases takes place in the middle tower or towers: in the first tower the acid is strengthened up slightly to near the limit theoretically possible, namely, 68 per cent. HNO_3. In the last tower the last traces of fume are absorbed.

The acid from the condenser generally has a specific gravity of 1·41 to 1·42 and contains 67 to 69 per cent. HNO_3: that from the towers is somewhat weaker.

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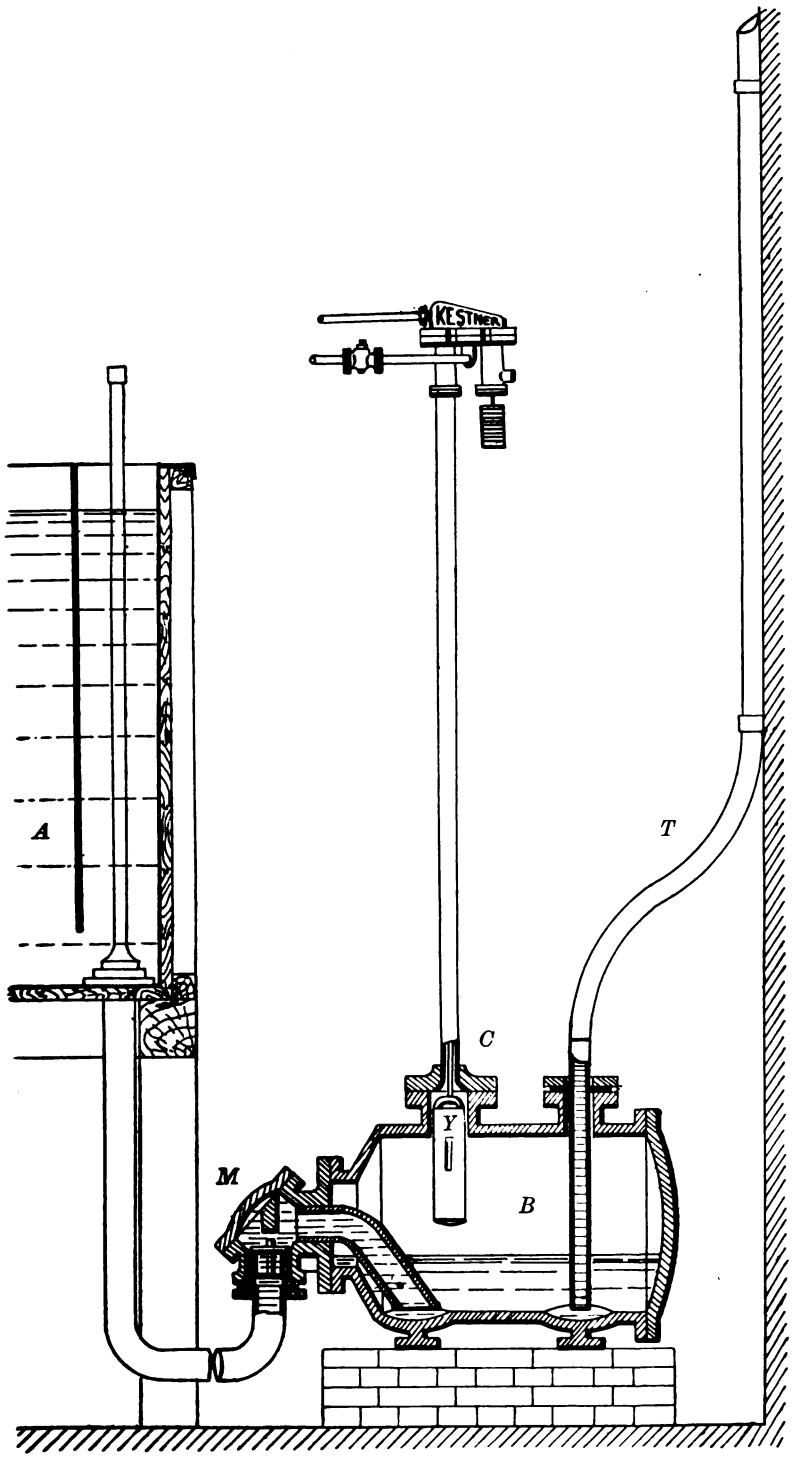

FIG. 24. Kestner Automatic Elevator or "Egg"

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MANIPULATION OF ACIDS

So far as possible acids of all sorts should be conveyed about the works in pipes and not in tanks, carboys or bottles. In a factory which makes its own acids and reconcentrates them there is no reason why these vessels should ever be used at all except in case of emergency. Wherever it is feasible the acids should run from one place to another by gravity, but of course this is only possible to a limited extent, and when the acid has come down to the ground level it is necessary to raise it again.

Materials. For strong sulphuric, mixed and waste acids, tanks, pipes and other appliances of either iron or lead can be used and last for a very long time. Iron is cheaper in first cost, but lead can be sold for a good price after it has been used; iron has the further advantage that it can be fitted up by any skilled workman, whereas lead can only be joined by a lead burner. Ordinary 2-inch wrought iron steam piping fulfils most of the purposes of an acid factory. Storage tanks can also be made of iron or steel boiler plates. Strong nitric acid has little action upon iron, but the dilute acid dissolves it rapidly. The vapour that rises from the surface of the acid is much more dilute than the acid itself, and where this condenses it is liable to attack iron strongly. Consequently it is better to use vessels and pipes of lead for this acid. Stone-ware is also used very largely with nitric acid. Aluminium is also sometimes used as a material of construction for acid plant, but in most cases possesses no advantage over iron or lead.

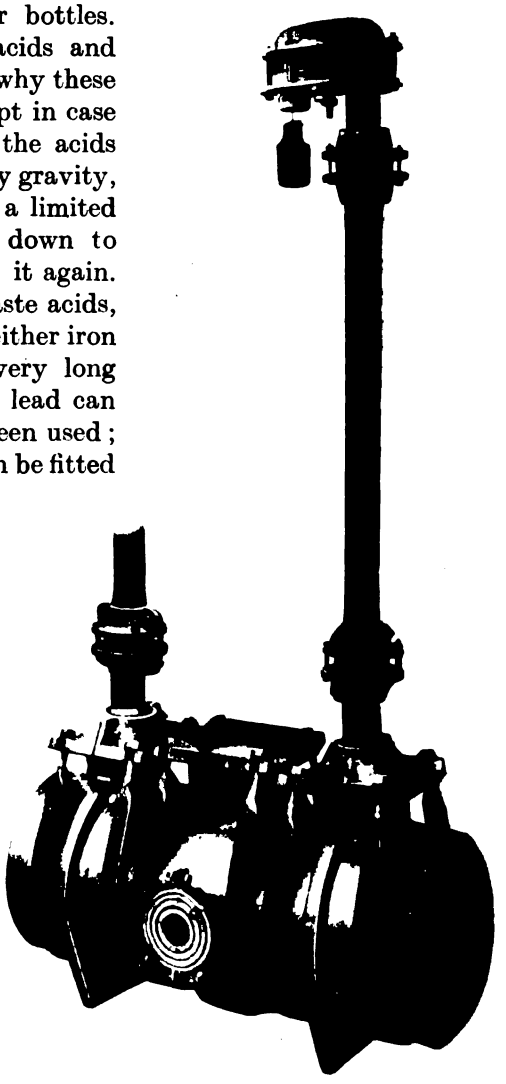

FIG. 25. Kestner Automatic Elevator for Nitric Acid

Where acids are running in a continuous stream the best appliance to

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use for raising it is an automatic egg such as that of Kestner, the construction of which is shown in Fig. 24. The liquid in the feed-tank, *A*, runs by gravity into the body, *B*, of the elevator or egg. As soon as the body is full the liquid raises the float, *Y*, which by means of the rod, *C*, closes the air exhaust valve and opens another valve which admits compressed air. The pressure closes the valve, *M*, and forces the liquid up the pipe, *T*, into a high-level tank. The air after delivering the liquid exhausts through the same pipe causing the pressure to fall and the valves to resume their former positions: the cycle of operations then repeats itself automatically in the same manner. These eggs can be obtained made of iron, with or without a lead lining, or of earthenware. Fig. 25 shows one type of the appliance specially devised for nitric acid. It can be fitted with a meter, which automatically registers the quantity of liquid that has been raised. A type of elevator is also made with a double body so connected up as to give a continuous stream of acid. **Eggs.**

Where the acid only has to be raised occasionally, a non-automatic egg can be used. This is simply a strong vessel made of one of the materials just mentioned and fitted with three pipes, one for the admission of the liquid, one for delivery, and one for air. The inlet and the air pipes are provided with valves which are operated by the attendant.

When acids have to be transferred from bottles, carboys or drums to a storage or mixing tank, they can be tipped in through a funnel placed higher than the top of the tank and connected with it by a pipe. In the case of oleum containing 60 to 70 per cent. anhydride there is some difficulty in consequence of the great volumes of most objectionable fumes that it gives off, especially as the acid has to be warmed to keep it liquid. The production of fumes can be almost entirely avoided by the following device: The drum of acid is raised to a platform above the level of the tank to which it is to be transferred, and a pipe is inserted through the bung-hole, the other end of the pipe going to the bottom of the tank. A vacuum is then produced in the tank by means of a steam-jet working through an ejector: as soon as there is sufficient vacuum the oleum starts to flow over, and will then siphon over by itself without any further assistance from the ejector. These ejectors can be obtained made of special acid-resisting alloys, but those made of ordinary iron withstand the mixture of steam and acid fumes quite well. **Oleum.**

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PART IV

NITRIC ESTERS OF CARBOHYDRATES

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CHAPTER X

THEORY OF NITRATION OF CELLULOSE

Stages of nitration of cellulose : Highest attainable nitration : Solubility : Soluble nitro-cellulose : Quantity of acid : Consumption of acid : Effect of nitrous acid : Temperature and time of nitration : Nature of the cotton : Nitro-cottons of low nitration : Pyroxylin : Collodion

Stages of nitration of cellulose.

CELLULOSE being a non-volatile colloid, all the ordinary methods of determining its molecular weight are inapplicable, and it is only possible to deduce it from a study of the compounds that it forms. At first the simplest possible formula was assumed for cellulose, $C_6H_{10}O_5$, and gun-cotton of high nitrogen percentage and low solubility in ether-alcohol was supposed to be formed by the substitution of three NO_2 groups for hydrogen atoms, $C_6H_7O_5(NO_2)_3$, and was consequently called trinitro-cellulose. The less nitrated product soluble in ether-alcohol was similarly supposed to be the dinitro-cellulose $C_6H_8O_5(NO_2)_2$. Later workers obtaining evidence of intermediate stages of nitration proposed to increase the formula of cellulose : Eder [1] doubled it, Vieille [2] quadrupled it, and Mendeléeff [3] octupled it, giving 48 atoms of carbon to each molecule, and hydrogen and oxygen in proportion. A nitro-cellulose having the composition of the above-mentioned trinitro-compound would contain 14·14 per cent. nitrogen. Quite as much as this has never been found by the analysis of any product that has ever been obtained, but various investigators by nitrating with mixtures of nitric acid and phosphorus pentoxide, or with concentrated sulphuric and nitric acids and extracting the product with ether-alcohol have obtained percentages between 13·9 and 14.[4] Lunge and Bebie [5] found that with mixtures of sulphuric and nitric acids the highest percentage of nitrogen was attained, not with anhydrous acids, but with mixed acids containing 11 or 12 per cent. of water : with a mixture in which the proportions $H_2SO_4 : HNO_3 : H_2O$ were 63·35 : 25·31 : 11·34 they produced a nitro-cotton containing 13·92 per cent. N, but this was not stable.[6] After keeping in the wet state it was re-analysed and found to contain

Highest attainable nitration.

[1] *Ber.*, 13, p. 169. [2] *P. et S.*, p. 2 ; *C.R.*, 95, p. 132. [3] *Moniteur scientifique*, 1897, p. 510.

[4] *See* Eder, Vieille, *loc. cit.* ; Hoitsema, *Ang.*, 1898, p. 173 ; Lunge and Weintraub, *Ang.*, 1899, p. 144. [5] *Ang.*, 1901, p. 514.

[6] It is of interest to note that the velocity of nitration of aromatic compounds dissolved in sulphuric acid is at a maximum when the molecular proportion of sulphuric acid to water is 1 : 0·7 or about 11·4 per cent. H_2O by weight. (Martinsen, *Z. f. physik. C.*, 1904, 50, p. 385.)

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then only 13·5 per cent. N, and other nitro-cottons nitrated almost as highly were found to decompose rapidly until the same composition was reached, even though the material was kept under water. This corresponds very closely with the formula $C_{24}H_{29}O_{20}(NO_2)_{11}$, endeka-nitro-cellulose. Hence the authors conclude that the molecule with 24 atoms of carbon fits the facts sufficiently well, but point out that this is only the lower limit of the possible size of the cellulose molecule, as to the real magnitude of which there is little or no evidence.

Hake and Bell, by nitrating filter-paper with a mixture of concentrated sulphuric and nitric acids in the proportion 3 : 1 for several days, obtained a percentage of nitrogen as high as 13·96, but their product was washed only with cold water, whereas Lunge and Bebie washed theirs for several days with hot water.[1]

With the possible exception of this endeka-nitro-cellulose no definite stages of nitration can be recognized : nitro-celluloses with every percentage of nitrogen from 7 to 13·5 and more can be produced, and those of the same degree of nitration may be soluble to very different extents in ether-alcohol. To characterize a nitro-cotton it is better to specify the percentage of nitrogen and the solubility rather than to state the number of NO_2 groups that it is supposed to contain in each molecule. The following Table shows the percentages of nitrogen and the volumes of gas evolved in the nitrometer by the different nitro-celluloses of the C_{24} series. The figures have been calculated using the latest atomic weights.

	Formula	C.c. NO per 1 g.	Per cent. N
Dodeka-nitro-cellulose . . .	$C_{24}H_{28}O_{20}(NO_2)_{12}$	225·6	14·14
Endeka-nitro-cellulose . . .	$C_{24}H_{29}O_{20}(NO_2)_{11}$	215·0	13·48
Deka-nitro-cellulose . . .	$C_{24}H_{30}O_{20}(NO_2)_{10}$	203·5	12·76
Ennea-nitro-cellulose . . .	$C_{24}H_{31}O_{20}(NO_2)_9$	190·9	11·97
Okto-nitro-cellulose . . .	$C_{24}H_{32}O_{20}(NO_2)_8$	177·3	11·12
Hepto-nitro-cellulose . . .	$C_{24}H_{33}O_{20}(NO_2)_7$	162·4	10·18
Hexa-nitro-cellulose . . .	$C_{24}H_{34}O_{20}(NO_2)_6$	146·0	9·15
Penta-nitro-cellulose . . .	$C_{24}H_{35}O_{20}(NO_2)_5$	127·9	8·02
Tetra-nitro-cellulose . . .	$C_{24}H_{36}O_{20}(NO_2)_4$	107·9	6·77

Nitro-cellulose containing up to 12·7 per cent. N can be obtained by nitrating with nitric acid alone, but only with difficulty, and the structure of the fibres is much damaged. In practice mixtures of sulphuric and nitric acid are always used. Various investigators have made numerous experiments to ascertain the effect upon the product of altering the composition of the

[1] *See J.S.C.I.*, 1909, p. 457.

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acid mixture. The results published by Bruley,[1] Lunge and Bebie (*loc. cit.*), and Saposhnikoff have been collected together by the last-named and plotted on triangular co-ordinates, the best method of representing the composition of ternary mixtures.[2] The numbers on the central line running from each corner (Fig. 26) represent not the percentages by weight but the molecular percentages, obtained by dividing the percentage by weight of each of the three constituents by its molecular weight, adding together the figures thus obtained and working out the percentages afresh. On the same figure Saposhnikoff has also given the vapour tensions, which have already been presented in another form in Fig. 22. It will be seen that for equal percentages of nitric acid the vapour tension is a maximum on the line joining the points marked HNO_3 and H_2O, H_2SO_4, or slightly to the left of it. This shows that when water is present in excess it combines with the nitric acid to form a less volatile compound, but on the addition of sulphuric acid this removes the water from the combination and combines with it instead. There is no evidence of any combination of the sulphuric with the nitric acid. The three curves, I, II, and III, indicate the degree of nitration of the cotton : the space inside curve I is the region of the endeka-nitro-cottons (about 13·5 per cent. N), that between I and II the region of the deka-nitro-cottons (12·8 per cent. N), and between II and III that of the lower nitrates with nine to six nitro groups (12 to 9 per cent. N) ; beyond curve III nitration is incomplete. It will be seen that the nitration curves follow a course similar to that of the vapour pressure curves : it seems that the compound HNO_3,H_2O has little action on cellulose and that the presence of sulphuric acid is required to set free the nitric acid from this combination before it can act.

Solubilities.

The percentage of nitrogen in a nitro-cellulose is the principal factor in determining the amount of energy that will become available when it explodes ; hence the importance of attaining a high degree of nitration. A very large proportion of the nitro-cellulose manufactured is afterwards converted into a dense colloid by treatment with a solvent, whereby the original fibrous structure of the cellulose is destroyed. The properties of this colloid and the nature of the solvent to be employed depend upon the solubility of the nitro-cellulose : hence the importance of determining this property. The solvent used for the determination is almost invariably a mixture of two parts of ether and one part of alcohol. The series of experiments by Bruley and Lunge and Bebie included determinations of the solubilities of the nitro-cottons. Their results are shown in Fig. 27 together with Saposhnikoff's nitration curves : inside the inner U-shaped dotted curve is the region of the collodion cottons completely or almost completely soluble in ether-alcohol. The nitro-cottons between the two curves have an intermediate degree of solubility,

[1] *P. et S.*, vol. viii., 1895–1896.

[2] Report of 7th Inter. Congress Applied Chem., Section IIIB., p. 41 ; *S.S.*, 1909, p. 442.

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10 to 90 per cent.; those outside the outer one are almost insoluble. It will be seen that the molecular percentage of water in the mixed acid is the principal

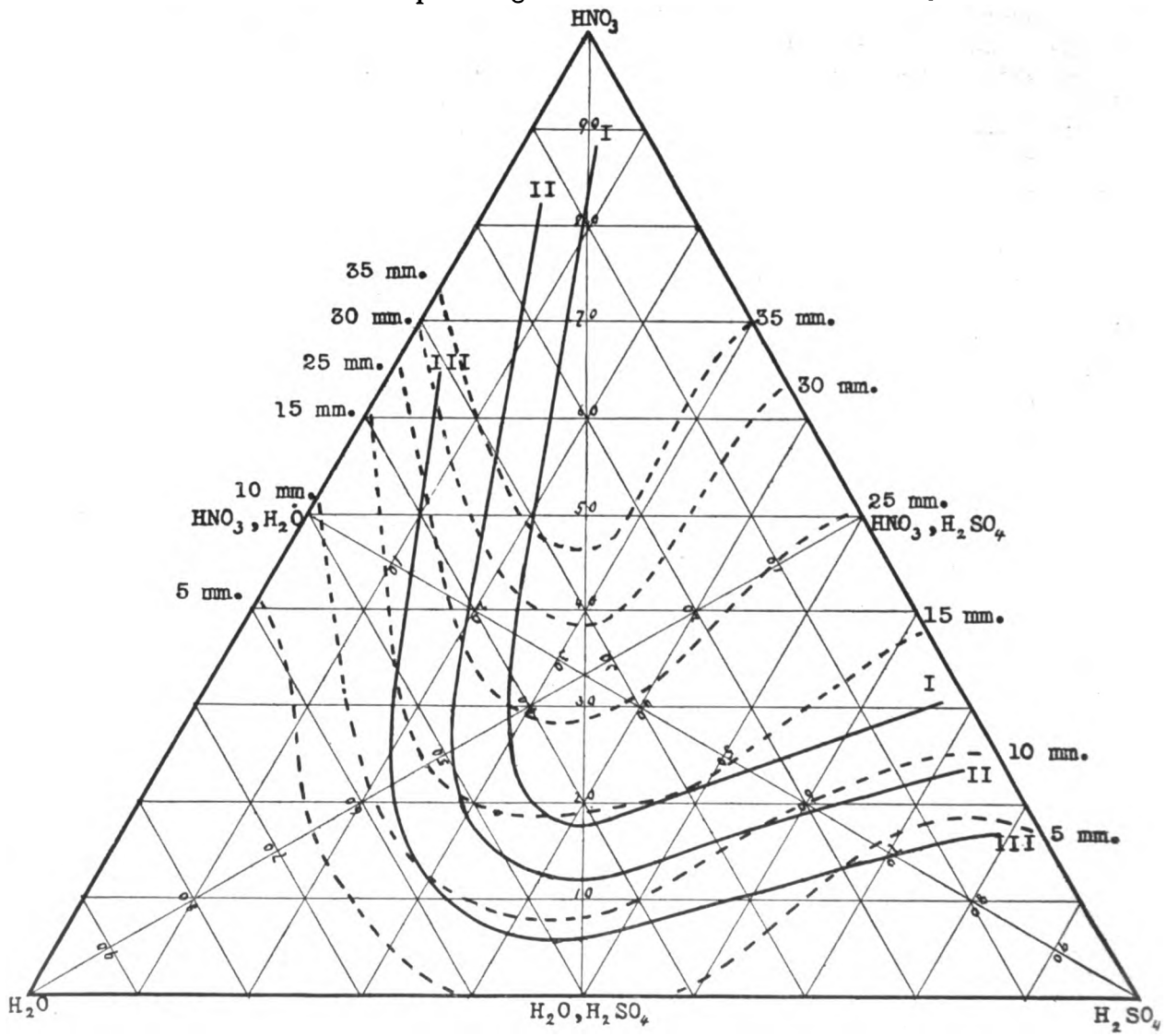

FIG. 26. Degree of Nitration of Nitro-cotton as a Function of the Molecular Composition of Mixed Acid and the Vapour Tension of the Nitric Acid

factor in determining the solubility. This diagram will be of assistance in determining what composition of acid is required to produce a nitro-cotton with any specified degree of nitration and solubility, but it must be remembered

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that it is based on laboratory experiments, which were carried out under very different conditions from those that prevail in the works.

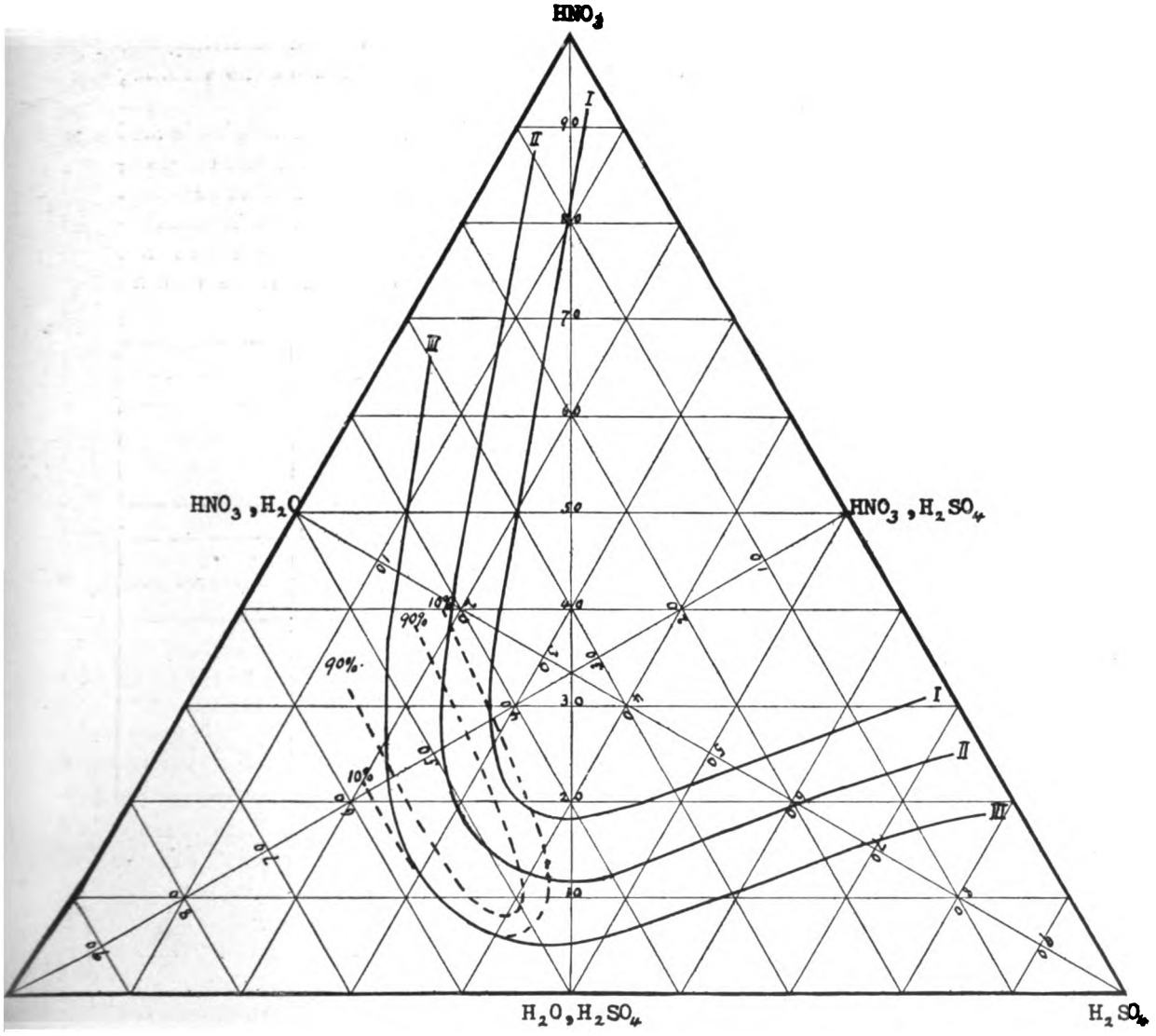

FIG. 27. Degree of Nitration and Solubility of Nitro-cotton as a Function of the Composition of the Acid

The cotton used for these experiments was generally cotton-wool, which is different in many respects to the cotton waste mostly used on the large scale : it is of much more open texture, each fibre being separated from the

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others, so that the acid can soak in very readily, thus facilitating the nitration. But as a result the material is very bulky, and for this reason inconvenient to use on a manufacturing scale, as it requires a very large proportion of mixed acid. Cotton-wool has often been subjected to a very drastic bleaching and scouring process, whereby the properties of the cellulose and of the resulting nitro-cellulose are injuriously affected.[1]

Soluble nitro-cellulose.

With acids containing a very large proportion of water or sulphuric acid nitration proceeds very slowly and is never complete. By raising the temperature of nitration this can be overcome to some extent, but then other reactions also take place : oxycellulose and nitro-oxycellulose are formed, and a considerable proportion of the cellulose is broken down altogether and passes into solution. Thus Lunge and Bebie obtained the results shown below with an acid of the composition :

	HNO_3	H_2SO_4	H_2O
Per cent. by weight . . .	42·15	38·95	18·90
Molecular per cent. . . .	31·7	18·8	49·5

Time of nitration	Temperature	Per cent. N	Solubility in ether-alcohol	Yield per cent.
4 Hours	17°	11·50	95·6	155
24 ,,	17°	11·58	99·8	156
4 ,,	40°	11·49	99·6	148
4 ,,	60°	10·81	99·8	52
¼ Hour	60°	11·46	99·7	147

The nitration was practically complete in four hours at the ordinary temperature ; there was only a slight increase in the nitration, solubility and yield, when the time was extended to twenty-four hours. Increase of the temperature to 40° diminished the yield somewhat, showing that the cellulose molecule itself was being attacked. At 60° in four hours this action was so strong that the fibres were entirely destroyed and the nitro-cellulose could only be recovered by pouring the acid mixture into water. When the time was cut down to a quarter of an hour this destruction of the fibre was much reduced. Lunge and Bebie found that with increase in the proportion of water there was an increase in the effect on the structure of the fibre. Up to 15 per cent. of water by weight in the acid mixture the structure appeared to be unaltered ;

[1] *See* Kilmer, *J.S.C.I.*, 1904, p. 967.

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but from 18 per cent. upwards the fibres were somewhat drawn together and the characteristic twisting of the cotton fibre disappeared. With a further increase in the percentage of water the structure was destroyed almost completely, the lumen was torn open, and the fibres disintegrated into small particles which were felted together forming little lumps. With 23 to 25 per cent. of water this destructive action attained a maximum; with still more dilute acids the fibres remained intact again, but on prolonged action they were broken down into smaller portions. By nitrating cotton with a mixture of H_2SO_4 35–46 per cent., HNO_3 35–45 per cent., H_2O 18–20 per cent. in the proportion of 30 of acid to 1 of cotton at a temperature of 40–50°, Claessen obtains a nitro-cotton entirely soluble in alcohol (96 per cent. by vol.) suitable for the manufacture of celluloid. (Germ. Pat. 163,688 of 1904.)

Mendeléeff and other Russian investigators have adopted a formula of the following form to express the effect of nitrating with acids of any particular composition: if the composition be written $2HNO_3 + aH_2SO_4 + cH_2O$, then the "characteristic" is m, which is equal to $(1 + a - c)$. Acid mixtures with $m > 0$ were supposed to give products of high nitration and low solubility, those with $m < 0$ soluble ones. Those in which the value of m exceeded -1 by only a little give soluble nitro-cottons with a maximum of nitrogen. If m lies between $-0{\cdot}3$ and $+0{\cdot}3$ the solubility is uncertain. If Fig. 27 be examined with reference to this formula, it will be seen that acids with equal values of m lie on a series of straight lines all passing through the point marked H_2O,H_2SO_4 in the centre of the base line. If $m = -1$ the locus of the points is the line running from the centre of the base line to the point HNO_3,H_2O. These acids contain the same number of molecules of water as of sulphuric and nitric acids together. It will be seen that this is indeed the locus of maximum solubility, but that the degree of nitration may vary considerably on this line. Apparently in order to get a product perfectly soluble in ether-alcohol it is necessary to have enough water not only to convert all the sulphuric acid into H_4SO_5, but also all the nitric acid into H_3NO_4. For $m = -1$ the locus of the points lies on the straight line going vertically upwards from the centre of the base to the apex.

Quantity of acid.

Nitration is affected to some extent by the proportions of acid to cotton, because during nitration nitric acid is used up and water is formed, so that the composition no longer remains the same. If the proportion of acid to cotton be very great the composition only alters slightly, of course. In the experiments on which Figs. 26 and 27 were based the proportions were generally 50 or 100 : 1, and the consequent alteration in position on the diagrams would only correspond to 0·5 to 1·5 molecular per cent. As a molecule of water is formed for every molecule of nitric acid used up, the molecular percentage of the sulphuric acid remains unaltered, and the point representing the

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molecular composition descends at an angle of 60° parallel to the lines marking the percentage of sulphuric acid.

Consumption of acid.

To produce a nitro-cellulose with 12·96 per cent. N, exactly one part by weight of nitric acid is used up for each part of cellulose, and 1·71 parts of the nitro-cellulose should theoretically be obtained. In practice the yield is as a rule very nearly equal to the theoretical. More generally the connexion between percentage of nitrogen and consumption of acid is given by the equations :

$$y = \frac{1400x}{63 + 45x}$$

$$x = \frac{63y}{1400 - 45y}$$

where x is the nitric acid used up in the nitration of one part of cellulose, and y the percentage of nitrogen in the nitro-cellulose formed.

Effect of nitrous acid.

Lunge with his co-workers, Weintraub and Bebie; investigated the effect of using nitric acid containing a considerable proportion of nitrous acid. They found that nitric acid containing as much as 6 per cent. HNO_2 gave as good yields, as high nitrogens and as low solubilities as acid free from this impurity. Even when the proportion of nitrous acid was higher than this, the effect was only slight. Lunge and Bebie also examined the stability of the products by determining the explosion points and the Abel heat tests. They came to the conclusion that the nitro-cotton made with acids containing nitrous acid is as stable as that made with acids free from it, but their results hardly bear this out. The tests were in all cases rather unsatisfactory, showing that the products had not been stabilized sufficiently : the Abel tests were no worse for the " nitrous " products than for the others, but with the explosion test the former gave slightly worse results in every instance. The true stability of a nitro-cellulose is very difficult to determine with certainty, unless it is very bad indeed ; it can only be ascertained by storage trials under various conditions extending over months or years. The evidence, such as it is, indicates that nitrous acid has a slightly bad effect on the stability. If the products had been thoroughly stabilized perhaps the evil effect would have been eliminated.

Temperature and time of nitration.

Lunge and Weintraub studied the influence of temperature and time of nitration of cotton wool with a mixture of concentrated sulphuric and nitric acids in the proportion 3 : 1, and found that with a rise of temperature the velocity of the action increases considerably.[1]

[1] *See also* Lunge, *J. Amer. Chem. Soc.*, 1901, 23, p. 527.

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Temperature	Time hours	Per cent. N	Yield per cent.	Yield (calc.)	Per cent. loss of cellulose
0°	½	10·71	152·3	153	Trace
0°	7	13·19	173·3	174	Trace
10°	7	13·37	175·8	176	—
15°	7	13·38	175·6	176	—
19°	½	12·72	166·1	170	—
19°	7	13·39	175·6	176	—
40°	½	13·07	172·3	173	Trace
40°	7	13·06	169·6	173	1·61
60°	½	13·08	169·2	173	1·95
60°	4½	13·07	162·1	173	5·67
80°	¼	13·07	161·2	173	6·52
80°	½	13·12	125·2	173	27·4
80°	3	13·12	81·5	173	52·8

It will be seen that at high temperatures the nitration proceeds rapidly to a maximum and then the yield falls again ; the cellulose is first converted quantitatively into nitro-cellulose, and if the action of the acids be prolonged the product dissolves partly, and the yield is consequently diminished. The part which is not dissolved is also attacked, with the consequence that the percentage of nitrogen is reduced. In the case of acids containing a considerable proportion of water this is demonstrated by the Table on p. 120, and is confirmed by the following figures, which were obtained by nitrating with concentrated acids at 32° :

Time of nitration		Per cent. nitrogen
5 Minutes	..	13·27
15 „	..	13·44
30 „	..	13·47
60 „	..	13·50
120 „	..	13·40

Further Tables show the influence of time with mixtures of concentrated nitric and sulphuric acids in different proportions :

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HNO_3	H_2SO_4	One-half hour		Twenty-four hours		Three days	
		Per cent. N	Yield	Per cent. N	Yield	Per cent. N	Yield
1	0	12·58	162·7	12·62	163·3	—	—
1	$\frac{1}{10}$	—	—	12·66	165·0	—	—
1	$\frac{1}{4}$	13·45	175·7	13·44	175·8	—	—
1	$\frac{1}{2}$	—	—	13·42	175·2	—	—
1	1	13·36	174·6	13·39	174·8	—	—
1	2	13·23	174·1	13·32	176·0	—	—
1	3	12·72	166·1	13·40	176·4	13·38	175·6
1	4	—	—	13·20	175·1	—	—
1	5	8·14	130·9[1]	13·10	166·6	—	—

HNO_3	H_2SO_4	Three days			Fifteen days		
		Per cent. N	Yield	Unnitrated cellulose per cent.	Per cent. N	Yield	Unnitrated cellulose per cent.[2]
1	6	12·63	162·4	0·85	12·74	169·8	None.
1	7	10·86	151·6	10·46	—	—	—
1	9	7·74	120·1	Much.	—	—	—
		Eight days			Thirty days		
1	8	10·88	144·6	10·7	11·70	152·0	4.48
1	10	5·43	65·0	41·1	—	—	—

These results indicate that when the proportion of sulphuric acid is increased the velocity of action is diminished. This applies not only to the nitration process itself, but also to the subsidiary actions. They show that it is not only cheaper but also better to nitrate with a mixture containing a considerable proportion of sulphuric acid, provided that the acid can be allowed to act on the cotton for some hours, but that if it be desired to obtain a high degree of nitration in a short time, as when nitrating in centrifugals, for instance, the proportion of nitric acid must not be too small.

Hake and Bell [3] found that the course of the nitration is greatly affected

[1] 25·4 unnitrated cellulose.

[2] The "unnitrated cellulose" was determined by treating the product with sodium ethylate solution. The authors use the term "unaltered cellulose," but the word "unnitrated" is preferable, because the cellulose is not unaltered, although it has not been nitrated to an appreciable extent.

[3] *J.S.C.I*, 1909, p. 460.

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by the physical form of the cellulose. If this be very dense, the acid cannot readily penetrate it, and the partly exhausted acid can only diffuse away and be replaced very slowly. Thus filter-paper is much slower in attaining its maximum degree of nitration than cotton-wool, and the thicker and denser the paper is the more is the nitration delayed. A larger proportion of sulphuric acid also combines with the more dense material.

Time of nitration	Cotton wool	Swedish filter paper Density 1	"Heat test" paper Density 1·22	Thick filter paper Density 1·52
	Per cent. N	Per cent. N	Per cent. N	Per cent. N
5 minutes	11·71	10·69	—	6·1
15 ,,	13·18	12·84	11·73	10·18
30 ,,	13·41	13·20	13·17	11·23
1 hour	—	13·35	13·38	12·52
2 hours	—	13·31	—	13·17
3 ,,	—	13·69	13·84	13·24
6 ,,	—	—	13·74	13·43
1 day	—	13·67	13·86	13·57
3 days	—	13·93	13·87	13·60
6 ,,	—	13·96	13·84	13·51
10 ,,	—	13·82	13·64	13·65
16 ,,	—	13·90	13·82	13·76

The acid used was a mixture of concentrated sulphuric and nitric acids in the proportion 3 : 1 ; the products were not stabilized but merely washed in cold water.

Nature of cotton.

In order to make sure that the cotton wool, which they used for their experiments did not give different results from other sorts of cotton, Lunge and Bebie carried out comparative nitrations with these different materials. The acid used had the following composition by weight : H_2SO_4 63·84 per cent., HNO_3 16·96 per cent., H_2O 19·20 per cent. ; the results were :

	Per cent. N	Yield
Cotton wool, chemically pure	11·76	159
American cotton (middling fair)	11·56	157
American cotton (Florida)	11·67	153
Egyptian cotton, white (Abassi)	11·69	155
Egyptian cotton, natural yellow quality	11·61	154

There is very little difference between the results with the different cottons ; the difference in the percentage of ash will account for a large proportion of what difference there is. The cotton wool contained only 0·05 per cent. ash, the other cottons about 0·5 per cent. The nitro-cottons were all completely soluble in ether-alcohol. The viscosity of the solutions was not determined ; in this respect there would no doubt have been differences.

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The above were all normal celluloses of good quality ; it is when abnormal celluloses are nitrated that differences are found in the yields and nitrogen percentages.

Nitro-cottons of low nitration.

Lunge and Bebie (*loc. cit.*) by nitrating with acid of the composition : HNO_3 37·17 per cent., H_2SO_4 34·41 per cent., H_2O 28·42 per cent. by weight obtained a nitro-cotton containing only 6·50 per cent. N, but the large amount of basic dye-stuff that it absorbed indicated that it was to a large extent nitro-oxycellulose. With nitric acid alone of specific gravity 1·4 (34·8 mol. per cent. HNO_3) a product was obtained, of which 62·9 per cent. was unnitrated fibre as determined by treatment with sodium ethylate : allowing for this the nitrated portion contained 4·00 per cent. N. It contained little or no oxycellulose or nitro-oxycellulose. When 5 per cent. of sulphuric acid was added to the nitric a product was again obtained which contained a large proportion of oxycellulose or nitro-oxycellulose ; there was about 58 per cent. unnitrated fibre, and the nitrated portion contained 5·12 per cent. N. Crane and Joyce [1] have nitrated cotton with acids containing little nitric acid and much sulphuric and water. With an acid of the composition :

	By weight		Molecular
HNO_3	9·0	..	6·4
H_2SO_4	65·5	..	30·0
H_2O	25·5	..	63·6

they obtained a product containing 3·51 per cent. N. It was insoluble in acetone, ether-alcohol, and all the other usual solvents for nitro-cellulose, but soluble in strong acids, caustic alkalis, and phenol. Ultimate analysis gave results agreeing with the formula, $C_{24}H_{38}O_{20}, NO_2 + 2H_2O$. It contained 0·34 per cent. sulphur and must therefore have been unstable. The composition indicates that it was a nitro-hydro-cellulose.

Pyroxylin.

Soluble nitro-cellulose or "pyroxylin" is used very largely outside the explosives industry for the manufacture of varnishes, photographic films, artificial silk, celluloid, etc. For practically all these purposes ready solubility is essential, and high viscosity generally a disadvantage. Therefore the nitration is usually carried out at a fairly high temperature, but it should not be too high, else the cohesion of the material is injuriously affected, and this is one of its most important properties. According to figures given by Worden,[2] Hyatt prepares the material for high-class celluloid by nitrating tissue paper with acid of the composition :

	By weight		Molecular
HNO_3	35.4	..	26·5
H_2SO_4	44·7	..	21·5
H_2O	19·9	..	52·0

[1] *J.S.C.I.*, 1910, p. 540.

[2] *Nitrocellulose Industry*, p. 113.

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The nitration is carried out at a temperature of 55° and lasts a half to one hour; there are 22 lbs. of acid per lb. paper. The product contains 11·0 to 11·2 per cent. N and about 0·1 per cent. ash; the yield is 140 per cent.

For commoner qualities a smaller proportion of nitric acid is used.

Collodion is much used in medicine to seal surgical wounds, for application to cuts and abrasions, and as a vehicle for the application of drugs to the skin when prolonged local action is required. The pharmacopœias of the various countries contain directions for the preparation of the pyroxylene for these collodions, but satisfactory or uniform products are not likely to be obtained by following them.

Collodion.

If the collodion cotton be of a suitable quality and it be dissolved in ether-alcohol together with camphor and castor-oil, the solution on drying will leave a film, which does not contract. In this way incandescent mantles are coated with material which enables them to bear transit. If the film were to contract on drying the mantle would be crushed, and when the collodion was burnt off the mantle would fall to pieces.

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CHAPTER XI

CELLULOSE

Nature of cellulose : Ligno-cellulose : Compound celluloses : Reactions of cellulose : With sulphuric acid : With nitric acid : Mercerized cotton : Viscose : Cellulose benzoates : Acetates : Schweitzer's reagent : Hydrate cellulose : Oxy-cellulose : Nitro-oxycellulose, etc. : Viscosity : Overbleached cotton : Nitrated mercerized cotton : Effect of dilute alkali ; Cotton used in manufacture : Action of bacteria : Structure of cotton fibre

Nature of cellulose.

COMPLETE knowledge of the nature of the process of nitration and the stability of nitro-cellulose would require a thorough acquaintance with the structure of the cellulose molecule, but in spite of numerous investigations there is still much that is unknown about the chemistry of this substance. There are few substances which are more complex, or about which it is more difficult to arrive at a definite conclusion. This is partly due to the fact that cellulose comprises whole series of allied substances, which are known by this name, and these are not all distinct from one another, but are liable to modifications, which cause one variety to merge gradually into another. Cellulose may be converted by reagents into products, such as oxy-cellulose and hydro-cellulose, which are very similar to the original substance in appearance and properties, and only differ from it very slightly in elementary composition. They are, however, somewhat more reactive, more liable to be attacked by chemical reagents. But true cellulose obtained from different sources also shows considerable variations, although no difference can be detected in the composition. Even the best cotton contains a proportion of material, which can be removed from it by treatment with bleaching powder and alkali, but the separation can never be carried to completion, because the treatment also attacks the true cellulose although to a less extent. The chemical behaviour of cellulose cannot be represented by a formula containing 24 or any other number of carbon atoms : in the nitration no definite stages or well-characterized nitrate can be distinguished ; on the contrary the nitration appears to be a continuous process from 6 up to 13·5 per cent. N. Cross and Bevan explain all this by the theory that cellulose consists of a " solution aggregate," that it is a solid solution in which substances of similar but not identical

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constitution are dissolved in one another Others consider that the union of these different constituents is more intimate, and is chemical rather than physical; that the cellulose molecule consists of a large number of smaller groups combined together, and that these groups may differ slightly from one another in configuration and even in composition. The whole subject of the chemistry of the colloids, of which class cellulose is such an important member, abounds with difficulties, and it is only recently that any considerable effort has been made to solve its problems.

Cellulose is the principal constituent of the framework or cellular tissue of plants; cotton and linen are almost pure cellulose, but can be further purified by judicious treatment, and are then characterized by their resistance to chemical action, as compared not only with most other organic materials but also with the allied cellulosic substances, such as ligno-cellulose, pecto-cellulose, and the products obtained by the action of reagents on cellulose, such as oxy-cellulose and hydro-cellulose. Cellulose has the empyrical formula $C_6H_{10}O_5$.

Of the ligno-celluloses jute fibre may be taken as a representative. It differs from cellulose by having a higher ratio of carbon to oxygen: **Ligno-cellulose.**

	C	H	O
Cellulose. . . .	44·37 ..	6·36 ..	49·27
Jute fibre . . .	46–47 ..	6·1–5·8 ..	47·9–47·2

By treatment with chlorine the "non-cellulose" can be removed, but even then the residual cellulose is more reactive than normal cotton cellulose and contains a considerable proportion of $-O.CH_3$ groups. It is supposed that cellulose is first formed in the plant, and is afterwards converted into ligno-cellulose. With the exception of a few materials, such as cotton, hemp, and to lesser extent ramie, practically all the vegetable fibres contain a considerable proportion of the non-cellulosic substance "pectose." In wood fibre the lignification has proceeded further than in jute. By treatment with alkaline sulphites a fairly resistant cellulose can be prepared, and this is now manufactured on a very large scale for paper-making, but the material thus obtained is more reactive than cotton cellulose. It has been used to a considerable extent for the manufacture of sporting smokeless powder, for which purpose a high degree of nitration is not so important as a thorough control of the rate of burning. Nitration experiments with jute were carried out by Mühlhaeuser,[1] using various mixtures of the concentrated acid. The fibre was purified first by boiling with 1 per cent. caustic soda solution.

[1] Dingler's *Pol. Jour.*, 1892, 283, p. 88.

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H_2SO_4 : HNO_3	Acids : fibre	Time of nitration (hours)	Yield per cent.	Nitrogen per cent.	
1 : 1	10 : 1	1	130	12·10	11·80
2 : 1	15 : 1	2½	132	12·26	12·04
2 : 1	15 : 1	3–4	145	12·03	11·96
3 : 1	15 : 1	3	136	12·03	11·80

Ligno-celluloses possess a number of characteristic reactions.[1] Salts of aniline colour the fibre a deep golden-yellow. Phloro-glucinol, dissolved in hydrochloric acid, gives a deep magenta coloration. Iodine is absorbed in large quantity, colouring the fibre a deep brown. The fibre readily combines with chlorine, as shown by the characteristic magenta coloration developed on the subsequent addition of sodium sulphite. Very characteristic is the reaction with ferric ferricyanide, obtained by mixing equivalent proportions of potassium ferricyanide and ferric chloride : the fibre is stained a deep blue and takes up a considerable quantity of pigment.

Compound celluloses.

Matthews [2] classifies the compound celluloses as follows :

(*a*) Pecto-celluloses, related to the pectin compounds of vegetable tissues ; represented among the fibres by raw flax ; resolved by hydrolysis into pectic acid and cellulose.

(*b*) Ligno-celluloses, forming the main constituent of woody tissue and represented among the fibres by jute ; resolved by chlorination into cellulose and chlorinated derivatives of aromatic compounds soluble in alkalis.

(*c*) Adipo-celluloses, forming the epidermis or cuticular tissue of fibres, leaves, etc. ; resolved by oxidation with nitric acid into derivatives similar to those of the oxidation of fats and cellulose.

The fibres of cork and other barks belong to the last class, but all such materials contain also large proportions of oils and waxes, tannins, ligno-cellulose and nitrogenous substances. Adipo-cellulose (or cuto-cellulose) contains a larger percentage of carbon than pure cellulose ; pecto-cellulose, on the other hand, has a high proportion of oxygen.

Reactions of cellulose.

With sulphuric acid.

Besides the nitro-celluloses produced by the action of mixtures of sulphuric and nitric acids, each of these acids alone yields products. Concentrated sulphuric acid chars cellulose and dissolves it, forming dextrine and, finally, glucose and other products of a comparatively simple nature. If the acid be diluted first with a third of its weight of water, the cellulose dissolves without charring with the formation of hydro-cellulose $C_{12}H_{22}O_{11}$, sometimes called amyloid, and cellulose-sulphuric acid $C_{18}H_{20}O_{10}(SO_3)_2$ (?) ; if the

[1] Allen's *Com. Org. Anal.*, 4th ed., vol. i., p. 434. [2] *Textile Fibres*, 1907, p. 221.

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action be only allowed to proceed for a short time and the cellulose be then washed, the surface is converted into a gelatinous non-fibrous film. In this way vegetable parchment is made. Cellulose combines very readily with sulphuric acid of moderate strength, but the compound formed undergoes further changes very rapidly. There is reason to believe that in the ordinary nitration process the cellulose first combines with the sulphuric acid, and that the product then reacts with the nitric acid to form nitro-cellulose.

Mixed esters with nitric and sulphuric acids.

Hake and Bell found, however, that a proportion of sulphuric acid always remains combined with the nitro-cellulose, and that the amount does not diminish below a certain amount when the time of nitration is increased. From this they concluded that in normal nitration the nitric acid reacts directly with the cellulose, and that the formation of the mixed esters is due to the absence of a sufficient amount of nitric acid, and the consequent intervention of some of the sulphuric.[1] But the evidence is inconclusive, as the compound first formed when cellulose is immersed in sulphuric acid is probably quite different from the mixed esters. (For further discussion of these mixed esters *see* p. 167.)

With nitric acid.

With concentrated nitric acid nitro-cellulose is obtained. Vieille[2] found the following percentages of nitrogen in the products yielded by acids of different strengths :

Molecular per cent. HNO_3		Per cent. N
80	..	12·7
75	..	11·5
67	..	10·2
57	..	9·0 dissolves in acid, reprecipitated with water.
40–42	..	7·0 friable mass.

With acid weaker than this very little nitration takes place ; Saposhnikoff, with an acid containing 34·7 molecular per cent. HNO_3, obtained a product containing only 1·46 per cent. N. Hake and Bell, with concentrated nitric acid, obtained nitro-cellulose with as much as 13·5 per cent. N.[3]

Labile nitrate.

Knecht[4] found that when cotton is immersed in weak nitric acid it swells up and forms a " labile " nitrate, from which the nitric acid can be removed again by washing with water ; if the cotton be in the form of yarn, a contraction of length takes place. To estimate the amount of acid retained by the cotton Knecht squeezed it out and then let it stand for several days in a vacuum desiccator over quicklime, then immersed it in water and titrated the acid removed. The following are some of the results that he obtained with acids of different strengths :

[1] *J.S.C.I.*, 1909, p. 457.
[2] *C.R.*, 1862, 95, p. 132.
[3] *J.S.C.I.*, 1909, p. 458.
[4] *Ber.*, 1904, p. 549.

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Nitric acid		HNO_3 retained by cellulose Per cent.	Contraction of yarn Per cent.
Molecular per cent.	Sp. gr.		
38·4	1·415	35·8	13·0
34·8	1·400	27·3	10·0
31·2	1.380	10·8	2·5
30·4	1·375	7·5	1·0
23·0	1·325	7·1	1·0

If cellulose be heated with acids of these strengths it is converted into oxy-celluloses, which contain a higher proportion of oxygen than cellulose does, and perhaps a lower proportion of hydrogen.[1]

Xyloidine. As mentioned above, Vieille found that cellulose was dissolved by acid containing about 57 molecular per cent. nitric acid. This matter has been more fully investigated by Jentgen,[2] who found that the most suitable strength for the preparation of these " xyloidines " at a temperature of 18° is 58·2 to 63·7 molecular per cent. (1·469 – 1·479 sp. gr.). When solution is complete it should be poured into a large volume of cold water. Products were thus obtained containing 6·2 and 7·2 per cent. N ; they were insoluble in ether-alcohol, amyl acetate and acetone ; ethyl acetate, cold acetic acid and acetic anhydride only caused them to swell up, but hot glacial acetic acid dissolved them. With slightly stronger acid a somewhat higher degree of nitration is attained, and the products are more soluble. A similar product may be obtained by dissolving cellulose in sulphuric acid and pouring into nitric acid, or by dissolving in nitric acid and pouring into sulphuric.[3]

Mercerized cotton. The formation of the labile nitrate of cellulose is very similar to that of the compound with caustic soda. If cotton be immersed in a solution of this alkali, it absorbs some of it, forming a combination in the proportion $C_6H_{10}O_5$, NaOH ; the cotton swells up, and if it be under tension it acquires a lustre resembling that of silk. The soda is removed again on washing with water, but the cotton is found to have changed in its properties, its tensile strength has become greater and it can be dyed more easily. This process is known as " mercerization," and is much used industrially ; for an investigation of it *see* Hübner and Pope, *J.S.C.I.*, 1904, p. 404. Many other reagents besides caustic soda and nitric acid produce much the same results, although not to the same extent as soda, *e.g.* solutions of sodium sulphide, potassium mercuric iodide, barium mercuric iodide and strong hydrochloric acid. Sulphuric and

[1] *See also* E. Knecht and A. Lipschitz, *J.S.C.I.*, 1914, p. 116.
[2] *Ang.*, 1912, p. 944.
[3] Haeussermann, *S.S.*, 1908, p. 305.

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phosphoric acids of certain strengths also react in the same way, but at the same time gradually dissolve the cellulose.

Viscose.

Cellulose treated in this way is much more reactive than untreated cotton. If to the mixture of cellulose and caustic soda solution carbon bisulphide be added, the material gradually swells up and eventually goes into solution, forming sodium cellulose xanthate. This solution can be made into fine threads by passing it through narrow jets, and if these threads are treated with alcohol and other reagents, the soda and carbon bisulphide are removed and a cellulosic material is regenerated. This is the basis of the Viscose artificial silk process.

Cellulose benzoates.

If the alkali cellulose be treated with benzoyl chloride, cellulose benzoates are obtained. Of these two are known: the monobenzoate (C_6) retains the form of the original cellulose; the dibenzoate is a structureless amorphous powder soluble in acetic acid and chloroform.

Acetates.

Cellulose acetates are formed by the action of acetic acid and acetic anhydride on cellulose that has been converted into hydro-cellulose by the action of strong acids or alkali. With unchanged cellulose there is little or no action. In this respect the formation of all other cellulose esters is essentially different from that of nitro-cellulose, for which the most resistant cellulose is best. The triacetate (C_6) has recently come into use on a large scale for making films for cinematographs, etc. It is soluble in chloroform, acetone and phenol. A tetracetate and other still higher derivatives were formerly supposed to exist, but the supposition was apparently founded on erroneous analyses.

Schweitzer's reagent.

Cellulose dissolves in a solution of copper hydroxide in aqueous ammonia known as Schweitzer's reagent. If the ammonia be neutralized, a cellulosic substance is regenerated. Pauly's artificial silk process is founded on this solubility. Cellulose also dissolves in a solution of zinc chloride and hydrochloric acid.

Hydrate Cellulose.

The cellulose regenerated from any of these solutions differs from the untreated material in being more reactive, and in containing a larger proportion of hydrogen and oxygen: the elementary composition agrees with the formula $C_{12}H_{20}O_{10}$, H_2O, or some mixture of this with normal cellulose. The treatment of cellulose with acids and alkalis yields very similar products, and those obtained by the hydrolysis of nitro-celluloses and other esters have the same characteristics. There are considerable differences, however, between celluloses which have been treated by the different processes. Cellulose, which has been mercerized and washed out, or has been converted into viscose and regenerated, is not so reactive, with Fehling's solution for instance, as cellulose that has been treated with acid. Cross and Bevan have proposed the name "hydrate cellulose" for the former; whereas the latter is called "hydro-cellulose." Hydrate cellulose gives off its extra water at a tempera-

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ture of 120°–125°, whereas hydro-cellulose retains its water obstinately, and at this temperature gives off less than untreated cellulose.[1]

Oxy-cellulose. By treatment with weak nitric acid, potassium permanganate, bromine, and other oxidizing agents a certain amount of oxygen is caused to combine with the cellulose, producing "oxy-cellulose," which also is more reactive than normal cellulose.

Nitro-oxy-cellulose, etc. The effect upon the nitration of the presence of these various abnormal celluloses has formed the subject of a number of investigations of recent years. Wichelhaus and Vieweg [2] found that mercerization does not affect the percentage of nitrogen, but considerably increases the solubility in ether-alcohol.

Berl and Klaye have treated cellulose with various reagents, nitrated them, and examined the products before and after nitration.[3] The following are the materials they experimented with:

I. Cotton wool treated with 2 per cent. soda solution to remove fat, and washed with hot distilled water until there was no alkaline reaction. By combustion analysis it was found to contain 44·38 per cent. C and 6·35 per cent. H calculated on the ash-free material: calculated for $C_6H_{10}O_5$ 44·42 per cent. C and 6·23 per cent. H.

II. Hydro-cellulose made by dipping the above in 3 per cent. solution of sulphuric acid, drying and heating for three hours at 70° in a closed vessel. Found 42·75 per cent. C, 6·43 per cent. H; calculated for $3C_6H_{10}O_5 + H_2O$ 42·86 per cent. C, 6·35 per cent. H.

III. Hydral-cellulose: 15 g. cellulose digested with 30 c.c.of a 30 per cent. solution of hydrogen peroxide for thirty days. Found 43·24 per cent. C, 6·25 per cent. H; calculated for $4C_6H_{10}O_5 + H_2O$ 43·24 per cent. C, 6·30 per cent. H.

IV. $KMnO_4$-Oxy-cellulose: 32 g. cellulose treated with a solution of 30 g. permanganate in 300 c.c. water for thirty-six hours with frequent shaking. Then decolorized with sulphurous acid and digested with dilute sulphuric acid. Dissolved in 10 per cent. caustic soda solution and reprecipitated with acid. Found 43·61 per cent. C, 6·30 per cent. H; calculated for $4C_6H_{10}O_5 + C_6H_{10}O_6$ 43·58 per cent. C, 6·05 per cent. H.

V. Br-Oxy-cellulose: 25 g. cellulose allowed to stand for a day with a mixture of 5 g. bromine, 75 g. calcium carbonate and 400 c.c water. The bromine was then driven off on the water-bath, 50 g. bromine and 75 g. calcium carbonate again added and the mixture shaken in a machine. Found 43·83 per cent. C, 6·31 per cent. H; calculated for $8C_6H_{10}O_5 + C_6H_{10}O_6$ 43·96 per cent. C, 6·11 per cent. H.

VI. $Ca(MnO_4)_2$-Oxy-cellulose: 5 g. cellulose allowed to stand for a week with 22 g. calcium permanganate and 1000 c.c. water, decolorized with

[1] *See* Ost and Westhoff, *C.Z.*, 1909, p. 197; *J.S.C.I.*, 1909, p. 325.
[2] *Ber.*, 1907, p. 441. [3] *S.S.*, 1907, p. 381.

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sulphurous acid and washed. The permanganate was added gradually. Found 43·52 per cent. C, 5·20 per cent. H; calculated for $3C_6H_{10}O_5 + C_6H_8O_6$ 43·51 per cent. C, 5·74 per cent. H.

VII. HNO_3-Oxy-cellulose: 50 g. cellulose heated on a water-bath for two and a half hours with 350 c.c. nitric acid of sp. gr. 1·3. Found 43·17 per cent. C, 5·95 per cent. H; calculated for $2C_6H_{10}O_5 + C_6H_8O_6$ 43·03 per cent. C, 5·98 per cent. H.

VIII. $KClO_3$-Oxy-cellulose: 30 g. cellulose heated to 100° with a solution of 150 g. chlorate in 3000 c.c. water and 135 c.c. hydrochloric acid (20° B.) gradually added. Found 43·34 per cent. C, 6·39 per cent. H; calculated for $3C_6H_{10}O_5 + C_6H_{10}O_6$ 43·37 per cent. C, 6·02 per cent. H.

IX. Bleaching Powder-Oxy-cellulose: cellulose allowed to stand in the air with a solution of bleaching powder of 10° B, washed with slightly acidified water, dissolved in 10 per cent. caustic soda solution and precipitated with acid. Found 43·62 per cent. C, 6·36 per cent. H; calculated for $4C_6H_{10}O_5 + C_6H_{10}O_5$ 43·58 per cent. C, 6·05 per cent. H.

These products were examined also as to the colorations they gave with various reagents, but these were affected to a considerable extent by the different physical structures of the materials.

	Ash per cent.	Methylene blue, mg. absorbed by 1 g.	Coloration with			Microscopic examination
			$I + H_2SO_4$	$I + ZnCl_2$	Fehling solution	
I. Cellulose . .	0·10	3·7	blue	blue-violet	7	Normal.
II. Hydro-cellulose	0·18	4·1	blue	blue	6	Fibres partly attacked, twisted.
III. Hydral-cellulose	0·16	6·5	blue	blue	4	Structure retained, interference colours.
IV. $KMnO_4$–O/c. .	0·96	4·4	blue	blue	7	Granular powder.
V. Br–O/c. . .	1·20	6·0	pale blue	blue	1	Structure almost destroyed, interference colours.
VI. $Ca(MnO_4)_2$–O/c.	0.77	6·7	pale brown	blue	5	Structure little changed, strength small.
VII. HNO_3–O/c. .	0·27	6·8	yellowish	blue	2	Structureless, hard grains.
VIII. $KClO_3$–O/c. .	0·32	9·5	yellow-brown	blue	1	Broken down, interference colours.
IX. Bleach. Pow.O/c.	0·55	8·1	pale blue	blue	3	Granular powder.

These products were nitrated with acid having the composition:

	Per cent. by weight		Molecular per cent.
H_2SO_4 . . .	46·22	. .	26·5
HNO_3 . . .	42·03	. . .	37·8
N_2O_4 . . .	·25		
H_2O	11·50	. .	35·7

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for twenty-four hours at a temperature of about 20°, after which they were washed for three days, first with cold and then with hot water. Ultimate analyses, etc., were made of the nitro-celluloses:

	Nitrogen by		Atomic ratios from analyses	Solubility in Et. Al.	Methylene blue test	Viscosity
	Nitrometer	Dumas	C : H : N : O			
I. Cellulose . .	13·50	13·32	24·0 : 34·0 : 11·0 : 41·8	1·8	0·6	10,000·0
II. Hydro-cellulose.	13·23	13·36	24·0 : 36·6 : 10·9 : 42·1	12·15	2·4	65·7
III. Hydral-cellulose	13·07	—	24·0 : 36·3 : 10·6 : 41·2	22·5	2·4	8·1
IV. $KMnO_4$–O/c. .	13·31	—	24·0 : 32·8 : 10·8 : 41·5	18·0	1·6	5·2
V. Br–O/c. . .	12.92	13·29	—	15·5	3·5	9·1
VI. $Ca(MnO_4)_2$–O/c.	13·25	—	24·0 : 35·5 : 10·8 : 41·4	20·5	3·3	11·1
VII. HNO_3–O/c.. .	12·87	13·28	24·0 : 34·0 : 10·4 : 40·0	34·0	5·0	7·9
VIII. $KClO_3$–O/c. .	13·04	—	24·0 : 33·9 : 10·2 : 40·5	18·0	3·0	7·2

The following were the results of the microscopic examination:

I. Fibres intact, in polarized light steel blue.
II. In polarized light grey fibres as well as steel blue.
III. Structure retained, in polarized light steel blue.
IV. In polarized light blue.
V. In polarized light blue together with many grey fibres.
VI. Fibres nearly intact, in polarized light blue.
VII. Grains, resolved by high magnification into separate fibres, in polarized light blue and translucent at the edges.
VIII. In polarized light blue with violet tinge.

In the case of No. VII the atomic ratio is calculated from the nitrogen determination by the Dumas method. The authors do not consider that any conclusions can be drawn from the differences in the nitrogen determinations by the two methods, because the quantities taken for analysis were in some cases very small. The increase in the solubility in ether-alcohol is no more than might have been expected from the lower percentage of nitrogen. The higher ratio of oxygen to carbon, which was to be observed in the unnitrated products after treatment, disappears in the nitrated products. The absorption of basic dye is higher, the viscosity much lower in the nitro-oxy-celluloses, etc., than in the nitro-cellulose. The viscosities were determined with 2 per cent. solutions in acetone by the method of Cochius (*see* p. 564). For comparison a number of nitro-celluloses were prepared by nitrating cotton with mixtures of equal weights of sulphuric and nitric acids, to which different proportions of water were added:

Viscosity.

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Per cent. water in mixed acid	Per cent. N in product	Methylene blue absorbed	Viscosity
11·50	13·50	0·63	10,000·0
13·20	13·02	1·74	578·0
15·49	12·48	2·43	503·0
20·53	10·41	3·19	56·0
25·31	9·09	3·66	15·0
Xyloidine	12·40	—	1·15
		Acetone	1·09

The xyloidine was made by dissolving in sulphuric acid and pouring into nitric acid.

The great fall in the viscosity of the solutions of nitro-oxy-cellulose as compared with nitro-cotton indicates that the size of the molecules has been much reduced.

In a later communication [1] Berl returns to the question of the effect of various treatment on the viscosity. Cotton which had been mercerized was nitrated with mixed acid of practically the same composition as that used by himself and Klaye; the product contained 13·5 per cent. N. This was dissolved in acetone, and the viscosities were compared with similar solutions from unmercerized cotton:

	Nitro-cotton from	
	Mercerized cotton	Unmercerized cotton
1 per cent. solution . .	14 ..	1·378 secs.
2 per cent solution . .	122 ..	22·080 secs.

Merely heating the nitro-cotton reduces the viscosity:

Gun-cotton, unheated	4·26 secs.
,, heated for 3 hours at 130° . .	1·47 ,,

Heating the cotton before nitration has a similar effect, especially if oxygen be present. The following were the viscosities of 1 per cent. solutions of the nitro-cottons in acetone:

Cotton dried but not heated	2330 secs.
,, heated 60 hours at 100° in atmosphere of oxygen .	463 ,,
,, ,, ,, ,, hydrogen	1063 ,,
,, ,, ,, ,, carbon dioxide	1110 ,,

[1] *S.S.*, 1909, p. 81.

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These matters are of some practical importance as different degrees of viscosity are required for different purposes.

The effect produced by heating in a current of dry oxygen indicates that oxidation takes place. Cunningham and Dorée [1] found that ozonized oxygen has a very powerful effect on moist cotton at the ordinary temperature, forming a peroxide of cellulose, which when boiled with water gave an oxy-cellulose with a copper value of 15 to 17.

Over-bleached cotton.

The nitration of cotton that has been over-bleached has been studied by Piest,[2] as also that of cotton that has been mercerized and heated to a high temperature. The experiments were done on a manufacturing scale and the nitro-celluloses were tested for stability. The results of the bleaching were as follows:

Experiment	Treatment	Fat	Ash	Wood-gum	Copper value	Consumption of N/2 NaOH
Standard	Normally prepared cotton . . .	·24	·37	0·92	1·85	1·6
Ia.	24 hours with bleaching powder solution of 3½° B	·15	·44	2·86	2·17	—
Ib.	48 hours with bleaching powder solution of 3½° B.	·10	·64	4·54	3·40	2·8
IIa.	8 days with solution of 2½kg. bleaching powder in 50 l.	·11	·60	8·13	10·73	5·2
IIb.	8 days with solution of 5 kg. bleaching powder in 50 l.	·19	·85	10·4	16·3	6·4

Of these materials Ia and Ib were white; IIa was yellowish-white and the fibres were short; IIb was yellowish and consisted of particles adhering tightly to one another. They were nitrated with acid of the composition:

	By weight Per cent.		Molecular Per cent.
HNO_3 . . .	20·5	..	20·2
H_2SO_4 . . .	69·0	..	43·6
H_2O	10·5	..	36·2

The time of nitration had to be varied in order to ensure that the acid had penetrated to the interior of the fibres in all cases. After nitration the material was washed first with cold and then with successive lots of hot water in a hollander.

[1] *J.C.S.*, 1912, pp. 497–512.

[2] *Ang.*, 1909, p. 1215.

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Experiment	Time of nitration	N	Solubility in			No. of hot washes	Stability	
			Ether-alcohol after		Absolute alcohol		B.J. method	Obermüller method
			First cold wash	Last hot wash				
	Hours	Per cent.					c.c.	mm.
Standard	½	13·07	—	6·0	2·40	7	3·4	119
Ib.	4½	12·84	18·8	26·8	4·75	27	8·3	148
IIa.	1	12·91	21·8	24·0	3·34	36	5·7	167
IIb.	2½	12·72	33·4	40·9	9·00	25	1·6	117

The number of hot washings required to obtain a satisfactory stability was much higher in the case of the bleached cottons, but as judged by the Bergmann-Junk test none of the nitro-celluloses was really stable except the last, for the official limit in Germany is 3 c.c., and a good gun-cotton does not give more than 2.

Similar experiments were carried out with mercerized cotton and cotton that had been heated at 150° in a current of CO_2: **Nitrated mercerized cotton.**

Experiment	Treatment	Fat	Ash	Wood-gum	Copper value
Standard	Normally prepared cotton . . .	·23	·28	1·44	1·77
IV.	Mercerized 20 minutes with 18·5 per cent. soda lye	·16	·25	0·21	1·59
VIa.	Heated 10 hours in CO_2 at 150° . .	·23	·23	1·52	1·69
VIb.	Heated 100 hours in CO_2 at 150° . .	·42	·25	2·44	2·29

The heated cottons were yellowish-white and yellow respectively. The following were the results of nitration:

Experiment	Time of nitration	N	Solubility in		No. of hot washes	Stability	
			Ether-alcohol	Absolute alcohol		B.J. method	Obermüller method
	Hour	Per cent.				c.c.	mm.
Standard	½	13·07	6·0	2·40	7	3·4	119
IV.	½	12·96	21·8	3·82	17	4·4	131
VIa.	¾	13·32	4·9	1·72	9	3·8	—

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Mercerization reduced the percentage of nitrogen only to a slight extent, but greatly increased the solubility in ether-alcohol and impaired the stability; it also increased the quantity of unnitrated material as determined by treating the nitro-cellulose with sodium sulphide solution. In the nitrated mercerized cotton this amounted to 1·8 per cent., whereas in all the others of the above products it varied between 0·6 and 0·8 per cent. Heating the cotton in carbon dioxide made very little difference to the nitro-cotton, but it was somewhat more difficult to stabilize.

The general conclusion from this investigation is that both over-bleaching and mercerization have a very bad effect on cotton intended for the manufacture of nitro-cotton.

Piest has also investigated the action of alkalis and ammonium sulphide solution on nitro-celluloses prepared from normal, over-bleached and mercerized cotton.[1] He found that the material from over-bleached cotton withstood these reagents less well than ordinary gun-cotton, but that the material from mercerized cotton withstood them somewhat better. The regenerated cellulose had a much higher copper value than the original cottons, whence Piest concludes that it has been converted into oxy-cellulose, but does not consider whether it may not rather be hydro-cellulose. Vignon[2] similarly found that nitrated hydro-cellulose was more attacked by caustic potash solution than normal nitro-cellulose, and nitrated oxy-cellulose still more.

Vignon[3] considers that ordinary gun-cotton is really nitro-oxy-cellulose. He prepared the product of maximum nitration according to Lunge's directions and made an elementary analysis of it. The results were in accord with the formula $3C_6H_7(NO_2)_3O_5 + C_6H_7(NO_2)_3O_6$. But this view is not generally accepted. The cellulose could only be oxidized by the nitric acid, some of which would be reduced to nitrous acid, whereas there is practically no formation of nitrous acid in the nitration process. Moreover, there are distinct differences between the nitration products of normal and oxy-cellulose.

Effect of dilute alkali.

As regards the effect upon cotton of treating it with dilute caustic soda lyes of different strengths and at different temperatures some curious observations have been made by Schwalbe and Robinoff.[4] They tried the effect upon pure cotton cellulose which had been prepared by Tamin's method[5] by boiling with a solution of resin soap and alkali without pressure, washing hot and bleaching very carefully; in this way they obtained a material which had a copper value of only 0·042.

[1] *Ang.*, 1910, p. 1009.
[2] *C.R.*, 1898, p. 1658.
[3] *C.R.*, 1902, p. 572.
[4] *Ang.*, 1911, p. 256.
[5] *Rev. mat. col.*, 1908, p. 313.

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Soda per cent.	Cotton dissolved	Copper values					
	Temp. 20°	Temp. 20°	Temp. 100°	Temp. 135°	Temp. 150°	Temp. 179°	Temp. 213°
0	—	·042	·109	·153	·190	·30	—
1	·74	·150	·180	·142	·10	—	—
2	·53	·166	·20	·17	·15	·11	—
3	·49	·195	·262	·395	·28	·128	—
4	·42	·257	·528	·89	·70	·445	—
5	·34	·135	·168	·285	·12	·05	0
7	·14	·154	—	—	—	—	—

When an over-bleached cotton is heated with water under pressure to a temperature above 150° there is a great increase in the copper value :

Temperature		Copper value
20°	..	·368
100°	..	·312
120°	..	·331
135°	..	·40
150°	..	·479
165°	..	1·43
179°	..	1·78
213°	..	3·43

The authors conclude that the strength of the soda used for the purification of cotton should never be allowed to fall below 5 per cent. and should be made up from time to time to this strength if necessary, also that temperatures above 150° should not be employed. They also found that the acid for subsequently acidifying need not be of greater strength than 0·1 per cent. ; with weaker acid the cotton is even whiter but the copper value is higher.

It has been found by Trotman [1] that the addition of neutral salts to soda lye considerably reduces the loss of weight of cotton boiled in it, and hence he concludes that the purification of the cotton is interfered with by the presence of these salts.

Cotton used in manufacture.

Von Lenk for his gun-cotton used cotton in the form of hanks of yarn. When Abel had discovered the very beneficial effect of pulping the gun-cotton there was no longer any object in using such an expensive variety of raw material, and he used instead cotton waste, the residual cotton from the spinning-mills. In the early days of the industry there was little demand for this material and the cotton waste supplied to the explosives industry

Cotton waste.

[1] *J.S.C.I.*, 1910, p. 249.

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was generally of good quality, but in course of time the demand for cotton waste not only for the manufacture of nitro-cotton but also for other purposes grew, and it is now difficult to obtain a really satisfactory cotton waste. Moreover, a special industry has sprung up—the cotton-waste industry—which collects the waste from all the mills and prepares it for various purposes. The object of the suppliers of cotton waste is to produce a material that will pass a specification, rather than to supply a really good cotton which can be made into stable gun-cotton, a matter of which of course they know little or nothing. Cotton waste for nitrating is made largely from the sweepings of the cotton-mills ; it contains some spun thread, but it is liable to consist largely of " fly," the fluffy material which escapes into the air during the various mechanical operations. This fly is the least resistant portion of the cotton as it is supplied to the mills. The presence of a very large proportion of dirt and oil and all manner of foreign matter makes it necessary to submit the cotton waste to a very drastic scouring and bleaching process, and this, as may be seen from the preceding pages, must inevitably produce a considerable proportion of oxy-cellulose and other modifications of the normal resistant cotton cellulose. At the same time more and more demands are being made upon the stability of the nitro-cottons, especially those used for the manufacture of smokeless powders for military and naval purposes. Consequently the explosives works have been obliged to give more attention to the question of their supplies of cotton. A few of the largest obtain their cotton waste unpurified and uncleansed from the mills and purify it themselves, and undoubtedly this is the best method where it is practicable.

Purification of cotton.

The cotton is subjected to various purification processes before it can be used. To remove the greater part of the oil and fatty matter it is either extracted with benzol, or is boiled with a dilute solution of caustic soda, or both. If the amount of oil to be removed is large, the former method is preferable, but there should in any case be a boiling with soda, as this removes a variety of other impurities. After this the cotton is well scoured by boiling with several changes of water. It is then generally bleached by treating it with a very dilute solution of bleaching powder or sodium hypochlorite ; this attacks various impurities, notably those that are coloured. After this it is treated with dilute acid to remove the last traces of bleach, and then well scoured again.

For the removal of the fatty matters, soaps, especially resin soaps, can be used. The whole purification process can be varied in many different ways, and must be adapted to the sort of cotton that is to be treated. It is required to remove all matters except normal resistant cellulose, without injuriously affecting the character of the latter. Although the methods of treating ordinary cotton goods have formed the subject of numerous investiga-

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tions, the preparation of cotton for nitration has not received the attention which its importance calls for.

Cop-bottoms.

For the manufacture of collodion cotton for blasting gelatine cop-bottoms are generally used. This is spun thread in a tangled condition, the last portion left on the spindle. This undoubtedly is a very good class of material, but is usually considered too expensive for the manufacture of smokeless powder.

Linters.

After the long staple fibres or "lint" has been removed by the first ginning, there is on American upland cotton seed still about 10 per cent. of short fibre cotton, which is recovered by a second process, and is known as "linters." From "sea-island" cotton, which is grown near the coast, and Egyptian cotton long staple fibres only are obtained, and consequently these varieties yield no linters. This would form quite good material for the manufacture of nitro-cotton, if it could be freed mechanically from the adherent resin and all particles of seed-husk, but this does not appear to be possible, and consequently the linters has to be submitted to a very drastic chemical treatment, which damages the cellulose. When nitrated it consequently gives low nitrogens and high solubilities in ether-alcohol. It is, however, used on a considerable scale in America and Germany, but not so much in England.

Tissue paper.

For the manufacture of collodion for high-class lacquers and celluloid, cellulose is used in the form of tissue paper. Although this is somewhat expensive, it has great advantages for this class of work: by inspection of the sheets it is possible to detect and then to remove every particle of foreign matter. Moreover, these thin sheets are nitrated completely in a very short time. The paper must, of course, consist of pure cellulose and should not be calendered.

Wood-cellulose.

For the preparation of shot-gun powders, cellulose is sometimes used which has been manufactured from wood fibre by the sulphite or one of the other commercial processes. A high degree of nitration is not required for "bulk" powders, but, on the other hand, a low rate of burning must be secured, and nitrated wood-cellulose gives this.

A number of wood and straw celluloses, and nitro-celluloses prepared from them, have been examined by Nitzelnadel.[1] The wood celluloses were prepared by the sulphite process, the straw celluloses by the sulphate process. None of the latter proved satisfactory, but one of the sulphite celluloses gave a good yield of nitro-cellulose, which could be rendered stable. The conclusion is therefore reached that wood cellulose prepared by the sulphite process can be made to give a material suitable for the manufacture of nitro-cellulose, but that it is quite likely that it will prove unstable unless the method of manufacture be carefully watched.

Action of bacteria.

Cellulose is attacked by various bacteria, especially if it be mixed with substances which provide food that favours their development. The methane

[1] *S.S.*, 1912, pp. 257, 301, 339, 384 and 409.

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which rises from marshes is apparently derived principally from the fermentation of cellulose ; the intestines of animals also contain bacteria and ferments, which attack cellulose. Even pure cotton cellulose can be thus entirely destroyed ; Hoppe-Seyler [1] found that Swedish filter-paper was completely resolved into gaseous products in the presence of river mud. He considered that cellulose was first hydrated $C_6H_{10}O_5 + H_2O = C_6H_{12}O_6$, and was then converted into methane and carbon dioxide, $C_6H_{12}O_6 = 3CO_2 + 3CH_4$. Omelianski [2] found two different ferments in river mud, one of which produced hydrogen, and the other methane.[3] The bacteria were anaerobic, but aerobic organisms capable of destroying cotton and linen have been found by Herson.

If cotton be stored for a long time under unfavourable conditions as regards heat and moisture, it is liable to be affected injuriously. In extreme cases it may become quite friable and dusty, but even before this stage is reached it is unsuitable for the production of stable nitro-cotton, probably on account of the formation of hydrated cellulose. If such a material be nitrated and stored for some time in a warm place it undergoes decomposition with the formation of a considerable amount of water and other decomposition products.

Structure of cotton fibre.

The micro-photographs (Fig. 28) reproduced from a paper by de Mosenthal [4] show very clearly the structure of the cotton fibre. In No. 1 the characteristic twisting of the fibre is seen ; Nos. 2, 3, 5 reveal the pores through the outer cuticle. No. 4, a longitudinal section of the fibre, is almost unique on account of the extreme difficulty of obtaining such a view ; it clearly shows the inner and outer cuticles and the matter in the centre of the tube. The material forming the greater part of the walls of the tubes consists of true cellulose. It is granular in structure and is held in position by the inner and outer cuticles, which exert so much pressure on it that the fibre is seen to be doubly refracting when examined in polarized light. If one of the cuticles be removed so as to relieve the pressure, colours are no longer seen under the polarizing microscope. When treated with dilute soda and bleaching solution, the compound cellulose of the outer cuticle is no doubt attacked to a considerable extent, but the inner cuticle and the matter in the interior of the tube cannot be reached so well by the solutions, and consequently must escape treatment. De Mosenthal observed that a single fibre has no capillary action, but when several are bundled together liquids are drawn up between them. This indicates that there is no free passage up the centre of the fibre ; that the tube is obstructed at intervals. The material in the centre of the fibre probably gives rise to unstable products on nitration, and it is perhaps the function of the pulping process to render it possible to remove these partly from the nitro-cotton.

[1] *Z. physiol. Ch.*, 10, p. 401.
[2] *C.R.*, 121, 1905, p. 653.
[3] *See also* Lafars *Handbuch der technischen Mykologie*, Bd. 3, Kap. 9.
[4] *J.S.C.I.*, 1904, p. 292.

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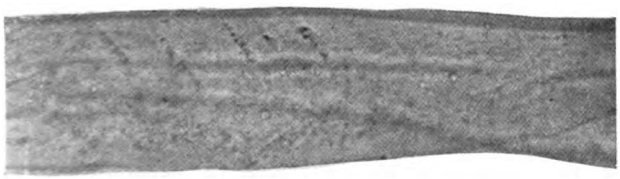
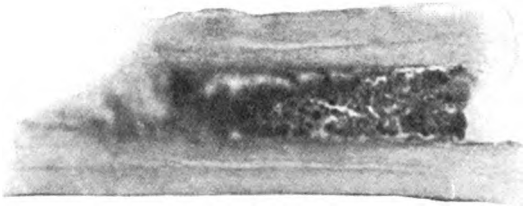
1. Natural Cotton Fibre × 300

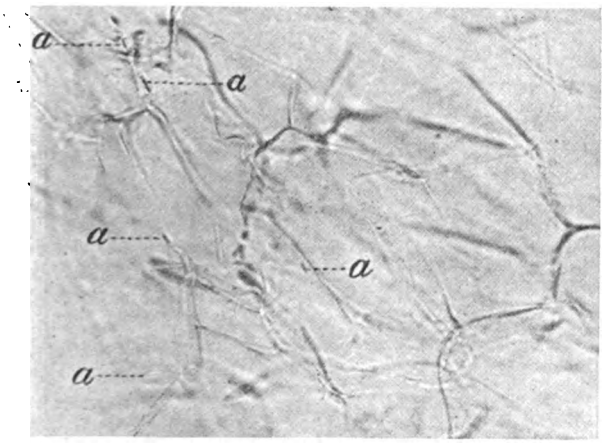
2. Portion of same Fibre × 1000



3. Portion of (2) Focussed to Show Stomata × 1000



4. Longitudinal Section of Cotton Fibre × 1000



5. Portion of a Fragment of Cotton Cuticle from a Solution in Cuprammonium × 1100

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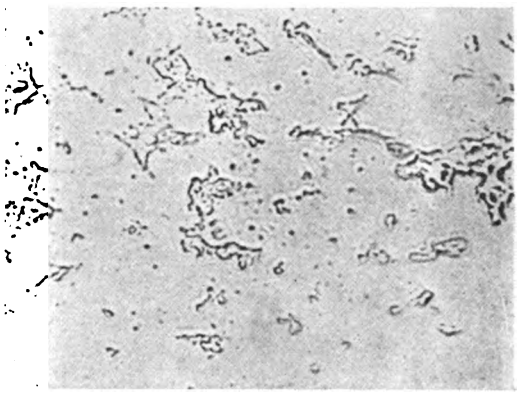
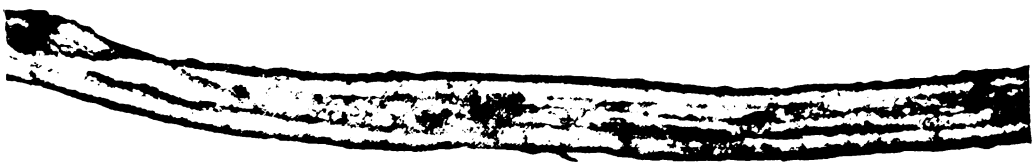


6. Granules from a 6½ per cent. Solution of Nitrated Cotton × 1500



7. Portion of a Nitrated Cotton Fibre × 300

FIG. 28. Microphotographs of Cotton (de Mosenthal)

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When treated with cuprammonium solution (Schweitzer's reagent), the cuticle dissolves much less readily than the bulk of the fibre (*see* No. 5, Fig. 28), and the same thing occurs when nitro-cotton is dissolved in acetone or other solvents. When passed through a Pasteur filter these particles of cuticle are removed from the solutions to a great extent. For the manufacture of artificial silk such filtration is necessary, because otherwise the orifices of the " silk-worms " get stopped up. It is somewhat remarkable that the molecules of nitro-cellulose, which must be very large, can pass through the minute pores of a Pasteur filter, which stop the molecules of many organic dye-stuffs. It can only be explained on the assumption that the cellulose molecule is in the form of a long string. The molecules of nitro-cellulose will not pass through a dialyser.[1]

When cotton is nitrated the pressure exerted by the cuticle is released, with the consequence that the twists of the fibres disappear (*see* No. 7), and the interference colours become much less brilliant. Similar changes in appearance occur when cotton is mercerized or submitted to other actions of a like nature.

[1] De Mosenthal, *J.S.C.I.*, 1907, p. 447.

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CHAPTER XII

MANUFACTURE OF NITRO-CELLULOSE

Picking the cotton : Teasing : Drying : Nitrating : Abel's process : Centrifugal process : Direct dipping : Displacement process : Hyatt nitrator : High nitrogen gun-cotton : Partially soluble nitro-cottons : Soluble nitro-cottons : Pyrocollodion : Collodion for blasting gelatine

Picking the cotton.

WHEN the raw material used is purified cotton waste, it is usually necessary to pick it over first by hand in order to remove all string, pieces of wood and metal, hard knots of cotton and all other matter which would not nitrate satisfactorily. This work is generally done by women.

Teasing.

Next the material must be opened out by means of a teasing machine. The simplest form of this consists of a rapidly rotating drum armed with numerous iron teeth and a pair of feed-rollers that grip the unteased cotton firmly and gradually feed it up to the drum, which tears it off in small portions and throws it out at the other side of the machine. The whole should be enclosed to prevent the fine cotton dust flying about.

Drying.

The cotton as supplied generally contains about 8 per cent. of moisture, and it is desirable to reduce this to about 0·5 per cent. This may be effected in any ordinary form of stove. The simplest type is a cupboard with a number of perforated shelves on which the cotton is placed, and steam-pipes underneath. Suitable openings allow hot air to circulate through the cotton and escape at the top of the cupboard. The disadvantage of this form is that the cotton in the lower trays gets much hotter and dryer than that in the top ones. Instead of having the steam-pipes underneath they may be in a separate heater through which air is forced by means of a fan and then through the stove, but the utilization of the heat is not very good, as the air is cooled down before it can take up more than a small proportion of water. In the most economical stoves these two methods of heating are combined, that is to say the air is blown through a heater into the stove, which is provided with a number of steam-pipes, which maintain the temperature at about 90° C. The cotton should be made to pass continuously through the stove by means of travelling bands. The drying takes about three-quarters of an hour. Over heating or too prolonged drying should be avoided.

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Nitrating. The method of nitration worked out by Baron von Lenk was described at length in the paper published by Abel in the *Proc. Roy. Soc.*, 1866, p. 269.[1] This was only slightly modified by Abel, and was followed at Waltham Abbey and in other factories until recently, the principal difference made being the use of cotton waste instead of the skeins of yarn used by von Lenk. The method as carried out at Waltham Abbey until 1905 was described thus by Sir F. L. Nathan :[2]

Abel's process. The nitrating acid was composed of three parts of sulphuric acid of 96 per cent. mono-hydrate to one part of nitric acid of 91 per cent. mono-hydrate, thoroughly mixed and cooled. This acid was run from the store tanks into cast-iron dipping pans, holding about 220 lb. each, the pans being supported in an iron tank through which cold water circulated to keep the temperature below 70° F. The dipping pans were provided at the back with gratings, on which to press out some of the acid from the charge. The charge of cotton waste weighed 1 lb. 4 oz., and on removal from the cooling box was passed from the back through an earthenware pipe in the partition running along the back of the pans, and raked by a dipper, as rapidly as possible, into the acid. After remaining in the acid bath for about eight minutes the cotton was removed to the grating, and a portion of the acid squeezed out by means of an iron lever having an iron plate attached to one end. After a charge had been removed from the dipping pan about 13¾ lb. of the mixed acid was run into it to replace the amount removed with the charge. The charge, now weighing with the adhering acid about 15 lb., was placed in an earthenware pot provided with a cover and transferred to the cooling pits, through which a stream of cold water flowed, and where it remained for twelve hours. During this period of digestion the conversion of the cotton into gun-cotton was completed. The contents of the pots were now emptied into a centrifugal wringing-machine, and the bulk of the waste acid extracted. The gun-cotton was then removed from the centrifugal machine and placed in galvanized iron pans with long handles. These pans when filled were carried quickly across to the immersing tank, and the gun-cotton thrown into a large bulk of water, the workmen standing by the tank and pushing the gun-cotton at once under the water with a stout wooden paddle. The immersing had to be done as quickly as possible, as, if the gun-cotton were allowed to come gradually in contact with water, it was liable to fume off. The immersing tank was fitted with a perforated copper plate to allow the water to overflow, so that fresh water was constantly passing through the tank. The gun-cotton was kept well stirred by means of a wooden paddle. When 2 cwt. had been

[1] This paper and Abel's later one on the Stability of Gun-cotton (*Trans. Roy. Soc.*, 1867, p. 181) are out of print and not always accessible but they have been translated into German by Dr. B. Pleuss and published by Friedländer, Berlin, 1907.

[2] *J.S.C.I.*, 1909, p. 180.

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immersed; the inflow of water was stopped and the tank drained down. When all the water had been run off the tank was filled up again with fresh water. This was repeated six times, or until the gun-cotton no longer tasted acid. When this stage had been reached the gun-cotton was wrung in a centrifugal machine, water from a hose-pipe being turned on the gun-cotton for one minute during the wringing, and it was then ready for boiling.

"This process, although it undoubtedly produced a good gun-cotton, had certain disadvantages, and the amount of labour required was very great. The plant, although individual items were not expensive, very rapidly deteriorated, and the cost of renewals and replacements was heavy. Power was required to drive the centrifugal machines, large quantities of water were used both for cooling and immersing, and decompositions, in the pans, pots, and acid centrifugals, were by no means infrequent."

In order to save the laborious and unpleasant operations of transporting the nitrating pots from the dipping pans to the cooling pits and from there to the acid centrifugals, and the transfer of the acid and cotton from one vessel to another a method has been adopted, especially in Germany, of nitrating in the centrifugal itself. A centrifugal machine used in this way lasts much longer than might be expected, for several years in fact with only occasional repairs. The firm which has had the widest experience in building this plant, Selwig and Lange, of Brunswick, has introduced several improvements in it. The basket of the centrifugal is fitted with a secondary driving gear, which can cause it to rotate slowly during the period of nitration, thus making the acids circulate, and their temperature can be kept at any desired point by means of a water jacket.

Centrifugal process.

The nitrating centrifugal is not very suitable for making gun-cotton of low solubility in ether-alcohol, because unless the cotton used is of good quality, parts of it will not be completely nitrated in the short time that it remains in contact with the acid.

The method of working is as follows: First, the acid is run into the centrifugal by turning on the cock on the pipe communicating with the supply tank. Then the cotton is immersed in the acid a little at a time until there is about 1 part of cotton to 50 of acid. The lid is then shut down and the nitration is allowed to proceed, usually for a quarter to three-quarters of an hour, according to the sort of nitro-cotton that is being made. Then the acid is allowed to drain away by a cock communicating with the waste-acid tank. The centrifugal is then rotated, slowly at first and gradually more rapidly until the proportion of free acid in the cotton has been sufficiently reduced. When making insoluble gun-cotton by this process it is generally desirable to leave not less than 1½ parts of free acid to every part of gun-cotton, because if the wringing be carried further there is danger of the charge fuming off, or even

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exploding.[1] With nitro-cotton of lower nitration the wringing can be carried somewhat further.

When the centrifugal has been stopped the nitro-cotton is taken out by means of tongs made of iron or aluminium, and removed to tanks where it is immersed in running water. Selwig and Lange have introduced an automatic hydraulic conveyor, the entrance to which is just by the centrifugal and may be seen at the back of Fig. 29. A ring of water jets directed downwards just below the opening immediately immerses the nitro-cotton as it is introduced, and the stream of water carries it along to a tank where the washing with cold water is completed. The somewhat dangerous operation of carrying the acid cotton in wooden boxes or other receptacles is thus avoided, and there is also a saving of labour.

During the operations of introducing the cotton into the acid and of removing the acid cotton after nitration, a considerable amount of acid fume is given off, and it is therefore necessary to provide the machine with a draught to draw the fumes away. Provision for doing this is shown on the left side of Fig. 29, where an upright earthenware pipe may be seen communicating with the interior of the centrifugal. This is intended to be connected by means of earthenware pipes with a stone-ware fan. I have found, however, that the draught produced in this way was very inadequate, and that the men who did the nitrating suffered much from the fumes which were not drawn away. A better arrangement was to make the lid of the centrifugal open to one side, and run a wooden shaft about 18 inches square along the back of the row of centrifugal machines with an opening just by each machine that could be closed with an aluminium door. At the other end of the wooden shaft there was an ordinary propeller fan with aluminium blades driven from a shaft. This created a much better draught with a smaller expenditure of power, and the cost of the arrangement was much less than that of the stone-ware fan, etc. The woodwork had to be renewed from time to time, but this was far less expensive than the repairs to the stone-ware fan had been.

Information about the various types of nitrating centrifugals will be found in a paper by Gründlich.[2]

Direct dipping. At Nobel's factory at Ardeer a method was adopted known as "direct dipping." According to a communication by Mr. Lundholm to Sir F. L. Nathan the process was as follows :

"The installation consists of parallel double rows of long iron tanks known as 'coolers.' Iron pots, termed 'dippers,' in which nitration is carried out stand in the coolers, sixty-two to each cooler. Sliding wooden covers rest

[1] At the K. B. Pulverfabrik at Ingolstadt the contents of a nitrating centrifugal exploded on July 1, 1911, killing one man and injuring another. The machine was being emptied at the time. It is supposed that it had been spun too long. As a rule the contents merely fume off. (*S.S.*, 1912, p. 60).

[2] *S.S.*, 1910, Nos. 18, 21, 22, 23, 24.

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on the coolers to guide the fumes from the dippers into earthenware pipes with openings at intervals, through which they are drawn by exhaust fans. The mixed acid, either cooled or warmed as necessary, is carried by lead pipes

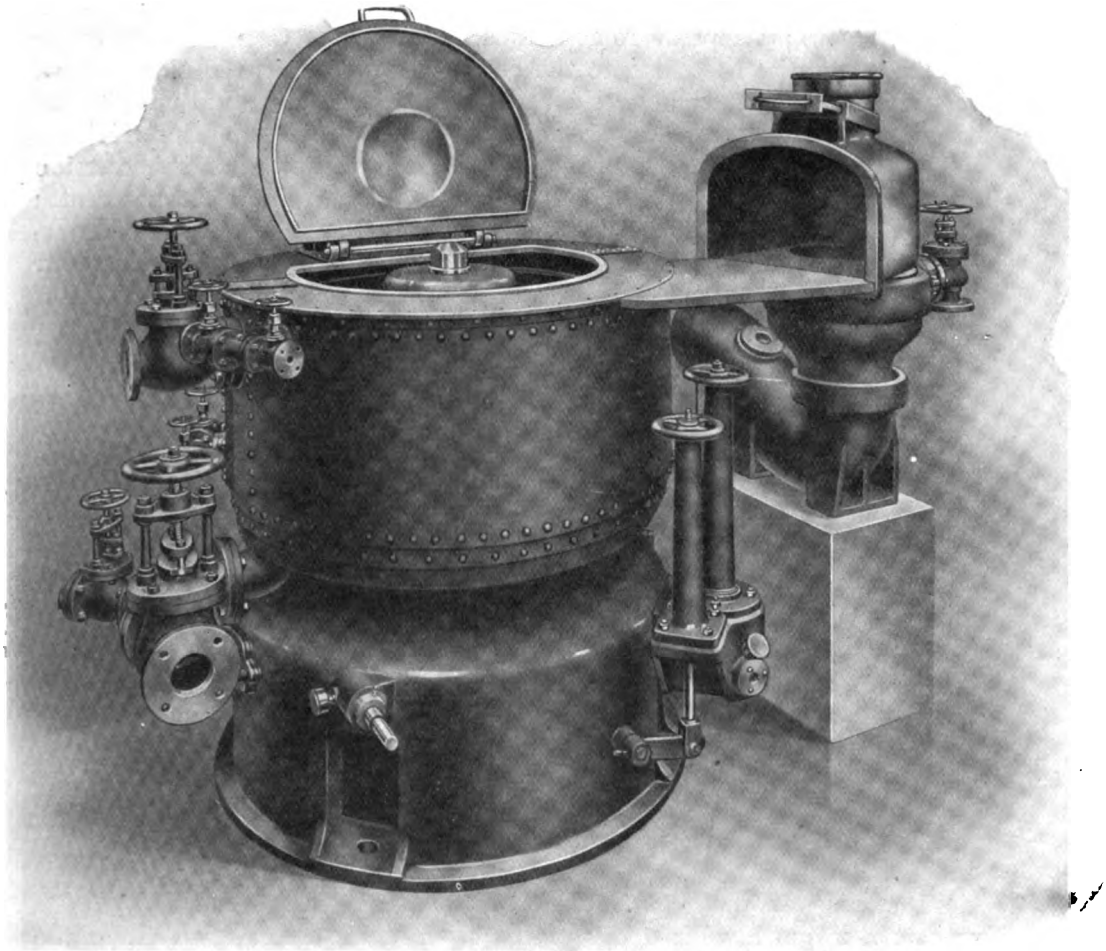

FIG. 29. Nitrating Centrifugal with Hydraulic Conveyor for the Nitro-cotton (Selwig and Lange)

placed between each row of coolers, and is supplied to the dippers through earthenware cocks at intervals.

"*Nitration.* The water in the coolers is kept at 15° C. The dippers, having been placed in position in the coolers, are each filled with 127 lb. of mixed acid by measurement from the acid taps; 4½ lb. of cotton waste are

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steeped in each dipper. To minimize decompositions each charge of cotton waste is added in about ten instalments. The wooden covers are only removed to allow steeping to be done, and are then at once replaced. The temperatures of nitration are: Initial temperature of mixed acid, 15° C.; maximum after steeping, 25° C.; temperature at end of nitration, 20° C. The duration of the nitration varies according to the output required from the plant. One, two, or three shifts may be worked per twenty-four hours, and the time of nitration may therefore be twenty-four, twelve, or eight hours respectively.

"The average composition of the mixed acid for a twelve hours' immersion is as follows: Sulphuric acid, 75·0 per cent.; nitric acid, 15.75 per cent.; nitrous acid, 1·30 per cent.; water, 7·95 per cent. For an eight hours' immersion a higher percentage of nitric acid and less water is used; for a twenty-four hours' immersion less nitric and more water. The average composition of the waste acid for a twelve hours' immersion is: Sulphuric acid, 77·8 per ecnt.; nitric acid, 11·0 per cent.; nitrous acid, 1·5 per cent.; water, 9·7 per cent.

"*Recovering the waste acid.* When the nitration is complete, the 'dippers,' covered with light aluminium lids, are placed on barrows, wheeled to the centrifugals situated at the end of the 'coolers,' and the whole contents tilted out into the centrifugals. Four dippers are loaded into each centrifugal, and the gun-cotton having been uniformly spread round the basket, the centrifugal is run for six minutes to remove waste acid. At the end of that time about 1 lb. of waste acid is still adhering to each pound of gun-cotton. The centrifugal cover, made of light aluminium, is not fixed to the centrifugal in any way, so that as little resistance as possible may be offered when there is a decomposition. This is the usual arrangement in the case of acid centrifugals. The cone of the centrifugal projects through a circular opening in the centre of the lid and is covered by a small loose aluminium box. Small holes are cut in the sides of this box, and are of service in warning the workmen when there is a decomposition, as fumes are generally seen to issue there first.

"*Drowning the gun-cotton.* When the waste acid has been removed, the gun-cotton is quickly lifted out of the centrifugals and thrown under the revolving paddles of the drowning tanks, which immediately immerse it. The men who do the discharging are provided with rubber gloves and wear thick flannel hoods, which completely cover the head, arms, and breast. The hoods are fitted with strong glass windows, and are connected by light rubber tubing to a supply of pure compressed air.

"*Pre-washing.* After a given quantity of gun-cotton has been drowned, the water in the tanks is run off and the gun-cotton thrown on to draining tables forming part of the drowning tank. It is then loaded into the pre-washing centrifugals, the acid water wrung out, and washed for a few minutes

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with cold water from a hose to remove adhering acid. No special precautions however, are taken to remove all acid at this stage. The bulk of the water having been removed, the gun-cotton is loaded from the centrifugals into bogies and conveyed to the boiling-house.

"The sixty-two dippers in each cooler form a 'charge.' Eight charges are worked by each shift. The yield is 159 per cent. of dry gun-cotton on the dry-carded cotton. The output per shift consisting of seventeen men is therefore: 4·5 × 159 × 62 × 8 ÷ 100 = 3549 lb.

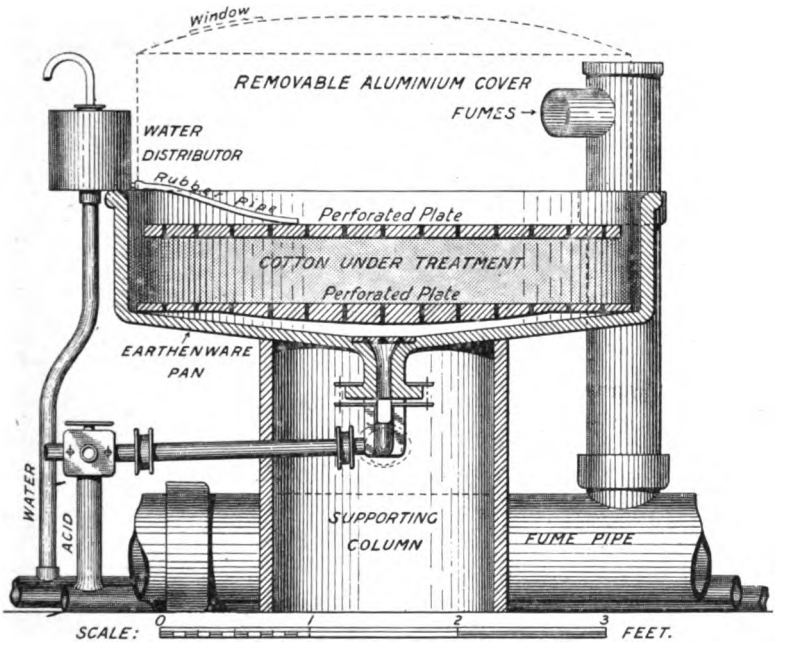

FIG. 30. Section of Displacement Apparatus (from *Arms and Explosives*)

Displacement process.

"Gun-cotton has been made at Waltham Abbey by Nathan and Thomson's displacement process since August 1905. The installation consists of a number of units of four pans worked together. The pans are of earthenware and circular, 3 feet 6 inches in diameter, and 10 inches deep at the side of the pan; the bottom has a fall of 2 inches to the outlet, which is $\frac{3}{4}$-inch in diameter. They are supported on earthenware pedestals about 1 foot 10 inches above the floor level. The four pans are connected together by lead pipes, and these are again connected to the nitrating acid supply pipe, to the strong and weak waste acid pipes, and to a waste water pipe, through a gauge-box, where the rate of flow is determined whilst the waste acids are

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being run off. Gravities of the acids are also taken in this box. The process proceeds as follows :

" A small perforated plate is placed over the outlet of each pan, and four per-

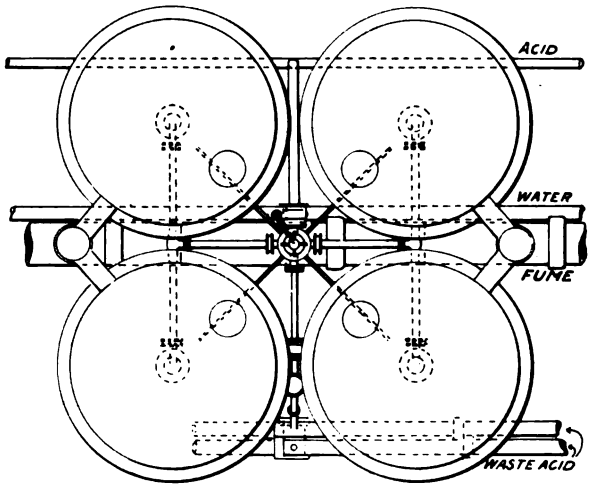

FIG. 31. A Unit of Four Pans (from *Arms and Explosives*)

forated segment plates making a complete disc about 1 inch less than the inside diameter of the pan, are placed on the bottom. Aluminium fume hoods, which are connected to an exhaust fan, having been placed on the four pans, the stoneware cock on the acid supply pipe is opened, and the acid allowed to rise

FIG. 32. View showing Arrangement of Units in Rows (from *Arms and Explosives*)

in the pans to the proper level. The nitrating acid is cooled in summer and warmed in winter, so as to maintain the same temperature of final nitration all the year round. The composition of the nitrating acid is 70·5 per cent. sulphuric acid, 21 per cent. nitric acid, 0·6 per cent. nitrous acid, and

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·9 per cent. water; the quantity in each pan above the bottom plates is 00 lb., and below the plates is an additional 50 lb. A charge of 20 lb. of cotton waste is then immersed in the acid, handful by handful, aluminium dipping-forks being used for the purpose. When all the cotton waste has been pushed under the surface of the acid, perforated plates in segments are placed on the top of it, care being taken that all cotton waste is below the

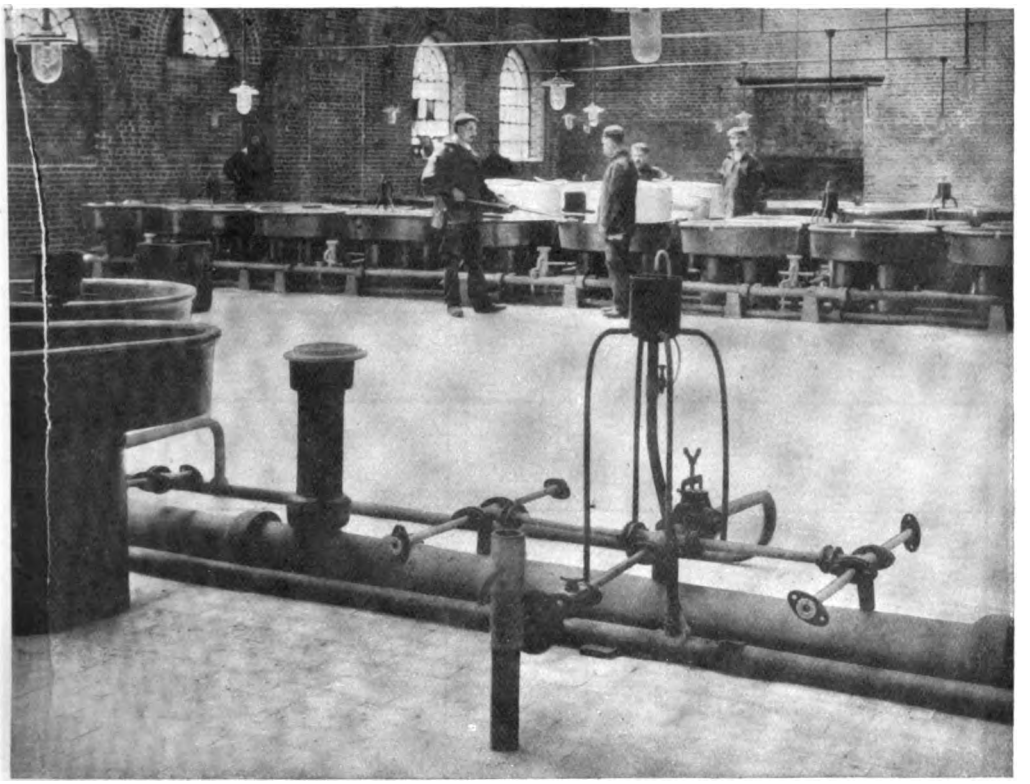

FIG. 33. Plumbing Installation for Displacement Plant (from *Arms and Explosives*)

surface of the acid, and a film of water at a temperature from 5° C. to 8° C. is run very gradually on the surface of the plates through a distributor. The film of water prevents the escape of acid fumes, and the fume hoods are then removed. The time required for dipping a charge is a quarter of an hour.

"The nitration is allowed to proceed for two and a half hours. At the expiration of this period the cock leading to the gauge-box is opened, and the waste acid allowed to run off at the rate of about 17 lb. a minute. Water, cooled, if necessary, is run on the top of the perforated plates, through the

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distributor, at an equivalent rate. The major portion, amounting to about 80 per cent. of the total waste acid, is returned to the acid store tanks to be revivified with Nordhausen sulphuric and new nitric acids The composition of this waste acid is 72·70 per cent. sulphuric acid, 17·30 per cent. nitric acid, 0·65 per cent. nitrous acid, and 9·35 per cent. water. The remaining 20 per cent. of the waste acid is sent to the acid concentration factory for denitration and concentration. The quantity of acid thus dealt with amounts to about 4 lb. for every pound of gun-cotton. Its composition is 61·0 per cent. sulphuric acid, 17·35 per cent. nitric acid, 0·55 per cent. nitrous acid, and 21·10 per cent. water. A small proportion of the water which follows the recoverable waste acid is slightly acid to the extent of 0·1 lb. for every pound of gun-cotton made. This is the total quantity of acid that is lost during the process. In the direct dipping and nitrating centrifugal processes the quantity of waste acid left in the gun-cotton is at least equal to the weight of the gun-cotton.

"The whole of the acid is displaced in three hours, and the water, which should fill the pan, is run through the gun-cotton, the gun-cotton drained down and sent over to be boiled. These operations occupy about an hour."

The following Table gives the principal figures in connexion with the four nitration processes described:

Process	Waltham Abbey Abel	Ardeer direct dipping	Dartford nitrating centrifugal	Waltham Abbey displacement
Acids, Analysis:				
H_2SO_4	74·0	75·0	69·35	70·5
HNO_3	18·0	15·75	23·15	21·0
HNO_2	0·6	1·3	—	0·6
H_2O	7·4	7·95	7·5	7·9
Quantity, lbs.	13·75	127	800–1100	650
Cotton waste, lbs.	1¼	4½	16–24	20
Acid per lb. cotton	11·0	28·2	50·0	32·5
Time of nitration, hours	12	12	1	2½
Yield on dry cotton, %	164	159	160	170
Output per man per week, lb.	458	1112	(3000)	1742

NOTE.—The output with nitrating centrifugals is not given in the original paper. It is approximately as stated.

The following are the principal advantages which the displacement process possesses over the Abel process, and over the direct dipping and nitrating centrifugal processes where they are similar to the Abel process:

(1) The displacement process takes the place of the processes of dipping, squeezing out excess acid, digesting in pots, acid centrifugaling, immersing, and water centrifugaling.

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(2) The actual dipping of the cotton waste is a very much less laborious operation—the heavy labour of squeezing out the excess acid is done away with ; the absence of fumes makes the work much healthier, and injuries to workmen from acid splashes are almost unknown.

(3) Loss of gun-cotton due to decomposition in the digesting pots and acid centrifugals, and consequent inconvenience and danger to workmen from nitrous fumes, are done away with, and the heavy loss from breakages of pots and lids is saved. Three and a half years' experience has proved that the earthenware pans are very lasting.

(4) Fumes during dipping, loading, and unloading acid centrifugals and immersing, are avoided.

(5) The quantity of acid lost is very much reduced. This reduction means also very much less pollution of the escaping washing water.

(6) The recovered waste acid is very much cleaner, a matter of the greatest importance from the point of view of revivification and concentration.

(7) The mechanical loss of gun-cotton in the acid and water centrifugaling processes, and in the immersing process, is saved.

(8) A more thorough preliminary washing of the gun-cotton is obtained with an expenditure of about one-fifth of the quantity of water, and less boiling, and consequently less steam, is required in order to reach a given standard of purity.

(9) Great saving in power is gained by the abolition of the acid and water centrifugals, and by the reduction in the quantity of water which has to be pumped.

(10) Renewals of plant, and repairs to plant and buildings are exceedingly low.

(11) The number of hands employed for any given output is much less—the total cost of labour being reduced by two-thirds.

(12) The yield is improved ; it averages 170 per cent.

(13) Finally, a more stable gun-cotton, of more uniform composition, is produced. It is also far cleaner and contains notably less mineral matter.

The last claim especially has proved to be amply justified. Cordite made from gun-cotton manufactured by the displacement process shows promise of lasting about twice as long under adverse climatic conditions, as that in which the Abel process was used, in spite of the fact that the latter would compare favourably with any other gun-cotton made except by the displacement process.

This improved stability is probably connected with a curious fact which has been observed by MacDonald.[1] He found that as the displacement proceeds, the percentage of nitric acid in the waste acid after falling slightly has a distinct rise and then falls again (*see* Fig. 34). The ratio of nitric to

[1] *J.S.C.I.*, 1911, p. 251.

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sulphuric acid also, after a very slight fall rises steadily until the end of the displacement and washing. This can only be due to a partial denitration of the gun-cotton, and evidently the more unstable products are decomposed to a greater extent than the normal stable gun-cotton.

The recovery of the waste acid is far more complete than by any other process, but, on the other hand, it is diluted somewhat with the water used for the displacement. Consequently a considerable plant is required for

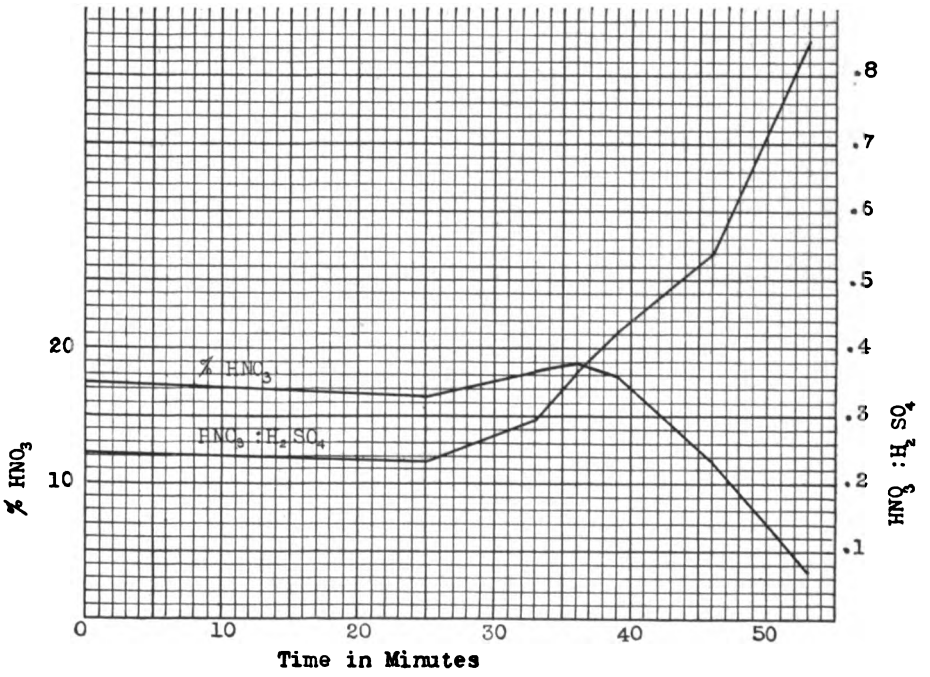

FIG. 34. Composition of Displaced Acids

working up the acids again and reconcentrating them. According to MacDonald the loss of acid is only 0·08 lb. per pound of gun-cotton produced but his own figures, as has been pointed out by Delpy,[1] indicate a very much higher loss.

Hyatt nitrator. According to Worden,[2] tissue paper for lacquers is nitrated in America in pots, which are placed on a rotating table, about which are arranged inlets for acid, a stirring apparatus, and a mechanism for tipping the pots into a centrifugal. The plant must be somewhat cumbersome and expensive, and is not likely to be adopted for the manufacture of explosives.

[1] *S.S.*, 1912, p. 237.

[2] *Nitro-cellulose Industry*, p. 110.

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High nitrogen gun-cotton.

The details given by Sir F. L. Nathan refer to the manufacture of gun-cotton containing about 13 per cent. N. If it be desired to obtain a product with a higher percentage of nitrogen, it is necessary to increase the proportion of nitric acid in the mixed acid (*see* Figs. 26, 27), but it is not very often that it is required to obtain a percentage much higher than 13, because such products are less stable and are more expensive to manufacture. It has been shown by Lunge and Bebie that beyond 13·5 per cent. the products are quite unstable (*see* p. 116).

Partially soluble nitro-cottons.

For the manufacture of various smokeless powders nitro-cottons partially soluble in ether-alcohol are used. The acid mixture to be employed depends upon the sort of cellulose and the method of nitration.

Soluble nitro-cottons.

For a nitro-cotton totally soluble in ether-alcohol there should, according to Fig. 27, be a molecule of water for every molecule of acid, whether nitric or sulphuric, but in practical manufacture a smaller proportion of water is generally used, especially if a high percentage of nitrogen is required. At one time it was thought to be impossible to prepare a totally soluble product containing more than 12 per cent. N. Mendeléeff, however, who worked at this subject from 1891 to about 1895, produced a soluble nitro-cotton with about 12·5 per cent. N, and he pointed out that a product with 12·44 per cent, contains just enough oxygen to convert all the carbon into CO and all the hydrogen into water. This material, which has been called pyro-collodion, was adopted as the basis of the Russian military smokeless powder, and later the United States adopted a powder made from a pyro-collodion containing about 12·5 to 12·7 per cent. N. This is produced by nitrating at a comparatively high temperature. According to Worden,[1] in Picatinny Arsenal the nitration is now carried out in Thomson's displacement plant. The acid has the composition :

Pyro-collodion.

	By weight		Molecular
HNO_3 . .	. 21–22	..	18·7
H_2SO_4 . .	. 63–64	..	36·3
H_2O . . .	. 15	..	45·2

The temperature is 30°–32°, and the charge in each pan consists of 20 lb. cotton and 700 lb. acid.

Collodion for blasting gelatine.

A high degree of nitration is also desirable for the collodion used for the manufacture of blasting gelatine and other similar high explosives, but the nitro-glycerine contains an excess of oxygen, and the proportion of collodion cotton is small, so that high power is not of the same importance as in the case of a military powder. The great essential is that the collodion cotton shall give a good stiff colloid with the nitro-glycerine. Other things being equal a cotton of high nitrogen will give a stiffer gelatine than one of low, but it will dissolve more slowly, with the result that the material will become

[1] *Nitro-cellulose Industry*, 1911, p. 97.

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stiffer on prolonged storage and less sensitive, and this may cause missfires. The percentage of nitrogen in collodion cotton for blasting explosives is usually between 11·5 and 12 per cent. The official definition of H.M. Inspectors of Explosives gives an upper limit of 12·3 per cent. It is of great importance that the cotton before nitration shall not be submitted to drastic treatment either with chemicals or heat, for this breaks down the molecules of cellulose and makes the blasting gelatine soft. For the same reason the nitrated product is not boiled, as is done in the case of gun-cotton, but it is treated for some days with water at a temperature of about 90°. The pulping also is not carried so far.

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CHAPTER XIII

THE STABILIZATION OF NITRO-CELLULOSE

Early methods : Boiling : Pulping : Removal of foreign bodies : Poaching : Blending : Addition of calcium carbonate : Moulding, etc. : The beater : Alkaline method of stabilization : Sulphuric esters : Velocity of hydrolysis of nitro-cellulose : U.S. Ordnance method : Cellulose nitrites : Products of decomposition : Washing collodion cotton

THE gun-cotton that was manufactured in the early days was purified by washing in cold water only, and it is principally to this very inadequate treatment that the numerous catastrophes of those times are to be ascribed. One of von Lenk's most important improvements was the introduction of a boiling of fifteen minutes with a potash solution of specific gravity 1·02. Sir F. Abel tried pulping the gun-cotton with the object of obtaining it in a more compact and convenient form. In his patent specification, No. 1102 of 1865, he says : **Early methods.**

"Now my invention has for its object to assimilate the physical condition of gun-cotton as nearly as possible to that of gunpowder by mechanically converting it into a solid conglomerate state, and imparting to it either a granular or other suitable form that will present the exact amount of surface and compactness required for obtaining a certain rapidity or intensity of combustion.

"I first convert cotton wool by the processes now well known into gun-cotton. For this purpose I prefer to use the cotton in the form of a loose roving. When the gun-cotton has been purified from acid by washing in running water and in very dilute alkali, I transfer it to a beating engine of the description commonly used in the manufacture of paper, where it is reduced to a pulp, which is then converted into solid masses. . . ."

Prolonged boiling with water, which is an essential feature of the modern process of stabilization, was not introduced until considerably later. Sir F. L. Nathan remarks[1] that : "Boiling as now understood did not form part of the process of gun-cotton manufacture when manufacture was started at Waltham Abbey early in 1872. About the middle of 1873, however, boiling vats were put up at Waltham Abbey, but no records exist, unfortunately, about the details of the early boiling processes. In the official **Boiling.**

[1] *J.S.C.I.*, 1909, p. 180.

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Notes on Gunpowder and Gun-cotton, published by the War Office in 1878, it is stated that gun-cotton manufactured at Waltham Abbey underwent two boilings by steam in wooden vats for eight hours each, the water being extracted after each boiling by wringing for three minutes in clean water centrifugal machines. The same boiling process was in use in 1888, according to a later edition of the same book. Five years later each boiling was extended to twelve hours, and the boiling lasted for five days and nights—that is, the gun-cotton received ten boilings of twelve hours each. In April 1894, this system of boiling was replaced by a system characterized by short boilings at the commencement of the process, the time of successive boilings being gradually increased. The scheme of boiling was as follows :

No. of boiling	Duration in hours	No. of boiling	Duration in hours
1	2	7	6
2	2	8	6
3	4	9	9
4	4	10	9
5	6	11	12
6	6	12	12

" This system of boiling was continued with but slight modifications until August 1905. On the introduction of the displacement dipping process it was found, as already stated, that gun-cotton made in this way was brought to a condition of stability by the boiling process then in use, and just referred to, at an earlier stage than gun-cotton made by the Abel process. A probable explanation of this fact is that during the displacement process a zone of acid liquid at a comparatively high temperature—somewhere about 40° C.—passes through the whole of the gun-cotton in the dipping pan. The action of this hot acid liquid may be to oxidize certain organic impurities which are certainly present, and to cause the breaking down of unstable nitrogen compounds into soluble or non-reactive bodies. Systematic experiments were therefore carried out, in 1905, to determine the most suitable and most economical method of purification by boiling for displacement process gun-cotton. In the principal experiments two types of boiling were employed—one in which long boilings were used at first, followed by short boilings ; the other in which short boilings were used at first, followed by long boilings. The following deductions were made from the results obtained in these experiments :

" (1) Purification of gun-cotton obtained by means of long boilings at the beginning followed by shorter boilings later, is superior to that obtained when the reverse condition holds. This is substantiated by the following

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considerations : Examination of the waters showed that neutrality is obtained earlier ; that less decomposition of the gun-cotton takes place ; that the stability, as shown by the various stability tests, is greater ; and that a stable condition is attained earlier.

" (2) A displacement washing after a long acid boiling at an early stage is a beneficial treatment. This treatment is probably responsible for the early attainment of neutrality.

" The system of boiling determined on as a result of these experiments was as follows :

No. of boiling	Duration in hours	No. of boiling	Duration in hours
1	12	6	4
2	12	7	4
3	4	8	2
4	4	9	2
5	4	10	2

with a cold water displacement wash after the first two boilings. A full account of these investigations was given by Dr. Robertson in a paper on the purification and stabilization of gun-cotton.[1] This system of boiling is still in use at the Royal Gunpowder Factory.

" The question of how the purification of gun-cotton can best be effected cannot, however, be considered as settled, nor can the system which has just been described, although it undoubtedly gives an excellent gun-cotton at the Royal Gunpowder Factory, be applied to gun-cotton made by other processes at other factories, without full investigations as to its suitability. Another matter which must be taken into account in connexion with the purification of gun-cotton by boiling, is the nature of the water available. The water at Waltham Abbey is very hard, and its alkalinity may be an important factor in the success of the boiling treatment in use there. This question is perhaps connected with another one, and that is, that the boiling of gun-cotton can be carried too far. The effect of boiling, whilst it no doubt breaks down impurities, also, no doubt, breaks down the stable ester itself. It is well known that if gun-cotton is boiled for a sufficiently prolonged period, the percentage of soluble matter will rise and the nitrogen-content will fall. The breaking down of ester will be accompanied by the formation of acid bodies, and the presence of alkali in the water will neutralize them and prevent them from reacting on the gun-cotton."

Since the above was written it has been found possible to reduce the time

[1] *J.S.C.I.*, 1906, p. 624.

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of boiling still further without affecting injuriously gun-cotton made by the displacement process.

Pulping. "On completion of the boiling process the gun-cotton is transferred to a beating engine somewhat similar to that employed for pulping the raw material used in the manufacture of paper. It consists essentially of a large iron roller armed with steel knives, and a bed-plate also provided with knives. The roller revolves, and as the gun-cotton passes between the two sets of knives, it is reduced to pulp of any desired fineness. As the pulping process proceeds, the roller is gradually lowered nearer to the bed-plate.

"Since the introduction of a thorough system of purification by boiling, Abel's original idea that the pulping and washing the gun-cotton received in the pulping process had a very material effect on its purification, no longer holds good to the same extent. At the same time there is no doubt that the very long staple gun-cotton before pulping retains in its tubes unstable bodies which no reasonable amount of boiling will remove. The effect of pulping is to reduce materially the length of the fibres and, at the same time, to produce a certain amount of crushing in them. This allows of impurities of an acid character in the tubes being removed, either mechanically or by diffusion.

Removal of foreign bodies. "After pulping, it is now customary to treat the gun-cotton in some mechanical way, in order to remove from it particles of metal, grit, and foreign bodies of a similar character. At the Royal Gunpowder Factory this is effected by running the gun-cotton pulp, suspended in a large volume of water, through grit traps, placed at intervals in a long shallow trough, the bottom of which is covered with blanket. The foreign bodies, being almost entirely heavier than the gun-cotton pulp, are retained in the grit traps, and the fine sand, also present in some quantity, is caught by the woolly blanket. An electro magnet in the last grit trap removes any magnetic particles passing the ordinary grit traps. It is surprising what a large quantity of foreign bodies are removed by these arrangements. In addition to grit traps and troughs, some factories use what is known as a knotter, the function of which is to remove small knots and any large pieces of gun-cotton which may have escaped complete pulping.

Poaching. "Washing the gun-cotton during the pulping is effected in some factories by the use of drum washers fixed to the beating engine; in the Royal Gunpowder Factory and other factories this washing is done in separate vessels termed 'poachers.' The poachers in use at Waltham Abbey hold about 10 cwt. of gun-cotton and 1100 gallons of water, and are fitted with power-driven paddles for agitation purposes. The gun-cotton receives at least three washings; it is allowed to settle down after each washing, and the washing water is removed by a skimmer. The washing water contains in suspension foreign bodies of a lower specific gravity than gun-

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cotton, and in the case of the earlier washing waters, there is always present a scum containing nitro-bodies of low stability.

Blending. "A further purpose served by poaching is the thorough blending of a number of different batches. This is a final blending, but at the Royal Gunpowder Factory there exists a regular system of blending right through the whole of the manufacturing processes. This system is briefly as follows: The cotton waste reaches the factory in consignments from different contractors. The waste is drawn from the store in proportion to the quantities on the contracts, and is mixed and passed through the teasing machine in these proportions.

"The next process where blending is possible is in charging the boiling vats. Two vats are filled simultaneously from a number of sets of pans—two pans of each set of four going into one vat; the other two of the set into the other vat. On completion of the boiling, four vats are emptied simultaneously into thirty-two beaters. This ensures the gun-cotton from the four vats being blended together in the beating process.

"On completion of the pulping the beaters are run alternately into the poachers in such a manner that the contents of the thirty-two beaters are blended into eight poachers. The gun-cotton in the eight poachers is therefore uniform throughout.

"The system produces gun-cotton of very uniform nitrogen-content. In 1907–1908, 291 tests, representing 600 tons of gun-cotton, gave the following nitrogen result":

Maximum	Minimum	Mean
Per cent. 13·05	Per cent. 12·93	Per cent. 13·0195

Addition of Calcium Carbonate. From the poacher the pulp passes to a "stuff-chest" or large tank provided with stirring arms. About this stage, if the gun-cotton is to be made into compressed blocks for blasting, stabilizing matters are added, usually calcium carbonate. If the water used be hard a considerable amount may be precipitated on the fibres by the addition of lime water. If the water be soft, or the quantity of calcium carbonate to be added be large, it may be added in the form of whiting.

Moulding, etc. To remove the great bulk of the water the pulp may now be passed into a centrifugal machine, lined with fine canvas. The damp mass thus obtained still contains 40 or 50 per cent. of water. It may be sent away from the gun-cotton factory in this form, or it may be moulded first into blocks. This is done by loading it into a hydraulic press, where it is subjected to a pressure of 30 or 40 lb. per square inch. Presses are also made which dispense with

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the preliminary wringing in the centrifugal machine. These have hollow plungers covered with fine wire gauze, and the bulk of the water is drawn off through these by the application of a vacuum. The hydraulic pressure is then applied whereby the gun-cotton is moulded into a block or cylinder, which can be handled conveniently.

The beater.

An important point concerning the beating engine is to secure a very good circulation of the water. In the machines used in the paper industry the rotation of the drum causes the water to move round so fast that the fibrous cellulose material cannot settle, but is carried round and round, so that it comes repeatedly under the knives, until it has been reduced to the

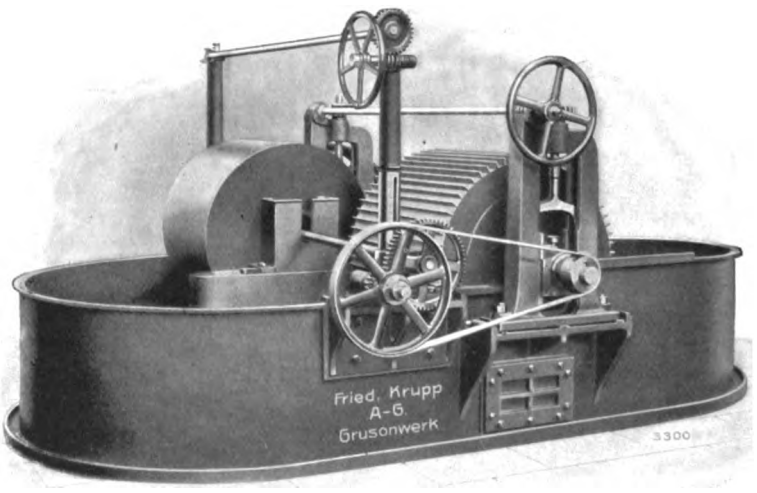

FIG. 35. Beater for Pulping Gun-cotton

required degree of fineness, and the machine requires very little attention. But if the same machine be used to pulp nitro-cotton, it is found that the solid material tends to settle down at the bottom, and it is necessary for a man to attend the machine and help the material round with a wooden paddle. This is not due entirely to the increase of the specific gravity, for that of nitro-cotton is only 1·67, whilst that of cotton is about 1·61, but in the nitration the weight of each fibre has increased about 70 per cent. The length has not become greater, probably it has diminished somewhat, consequently each fibre has become much stouter, as may be seen clearly on comparing micro-photos 1 and 7, Fig. 28. There is therefore much more weight for the same amount of surface, and consequently the material is borne along by the water with greater difficulty.

A good form of beater is that of Hoyt, in which the material is made to

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circulate vertically instead of horizontally. The drum carries the water and pulp right over, after which they descend a steep incline, then another under this sloping in the opposite direction to the lowest point of the knife drum.

The fixed knives under the rotating drum require to be sharpened frequently, and it is usual to have a duplicate set. The knife-blades on the drum also require sharpening from time to time. They thus become gradually shorter, and this causes the circulation of the pulp to become worse.

Alkaline method of stabilization.

The development of the method of stabilization took a somewhat different course in some factories; a boiling process has been introduced, after the pulping, and was carried out in large iron tanks fitted with stirring gear and valves for running off the water at different levels. The water had to be kept alkaline throughout the operations, else the acid developed by the nitro-cotton would attack the iron of the vessels. At first sight it appears as though the boiling in the pulped state must purify the material much more effectually than when the material is compact, but experience has proved that this is not so. Robertson has shown that the most important part of the purification is the boiling with dilute acid, and in the alkaline method this is omitted altogether. Actual tests and trials have shown that the gun-cotton stabilized by this process is distinctly inferior to that prepared by the Waltham Abbey process.

Sulphuric esters.

The reason for this, or at least one reason, was revealed by the observation of Cross, Bevan, and Jenks, that mixed esters containing both sulphuric and nitric acid residues are liable to be formed when cellulose is immersed in the mixed acids.[1] The observation was confirmed by Hake and Lewis,[2] and was further investigated by Hake and Bell.[3] When these products are allowed to stand they gradually become acid in consequence of the formation of free sulphuric acid, which may ultimately lead to the spontaneous explosion of the gun-cotton. Hake and Lewis suggested that the disastrous explosion at Stowmarket in 1871 was probably caused by the presence of sulphuric esters.

It was shown by Robertson[4] that the sulphuric esters are decomposed hydrolytically by boiling with acid water much more rapidly than with alkaline water; in fact treatment with alkalis seems to fix the sulphuric group firmly into the product. This behaviour is very similar to that of the cellulose aceto-sulphates, which have been investigated by Cross, Bevan, and Briggs.[5] They found that even under the action of cold distilled water the sulphuric acid residue of these mixed esters was gradually split off, but much more rapidly in boiling water, whereas on treatment with alkaline solutions the whole of the acetic acid residue could be eliminated by saponification, whilst the combina-

[1] *Ber.*, 1901, p. 2496; *Researches on Cellulose*, vol. ii., p. 51.
[2] *J.S.C.I.*, 1905, pp. 374 and 914.
[3] *J.S.C.I.*, 1909, p. 457.
[4] *J.S.C.I.*, 1906, p. 624.
[5] *Ber.*, 1905, pp. 38 and 1859.

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tion between the cellulose and the sulphuric acid remained intact in the form of a cellulose sulphate. This behaviour was explained by the fact that the sulphuric acid residue in these esters exists in the form of $-SO_4H$, which is readily hydrolysed by the action of water or acids, but becomes $-SO_4M$ in the presence of alkalis, towards which it is remarkably stable.[1] It has been possible to study the aceto-sulphates more thoroughly than the nitro-sulphates because a larger proportion of sulphuric acid can be made to combine in the former case.

It was shown by Robertson [2] that the sulphuric esters are eliminated more rapidly from the gun-cotton if the first boilings are long, that is not less than twelve hours each, than if they are short. The reason is that under these conditions the material is in contact with hot dilute acid for a considerable time, whereas if the water be renewed constantly, the alkalinity is restored each time, and this impedes the saponification of the sulphuric esters.

Velocity of hydrolysis of nitro-cellulose.

Although the sulphuric esters are hydrolysed so much more rapidly by acid than alkali the reverse is the case with the nitric esters. The velocity with which a nitro-cellulose containing 12·84 per cent. N is hydrolysed by solutions of barium hydrate at a temperature of 39° was measured by Silberrad and Farmer.[3] They found that the velocity is given by the equation: $q(s - v) = kv$, in which q is the quantity of nitro-cellulose in grammes per 400 c.c. of the solution, v is the observed velocity with which the alkalinity of the solution diminishes measured in gramme-equivalents per litre per hour, s is the limiting velocity for a solution saturated with nitro-cellulose, and k is a constant. Further, as the velocity is proportional to the concentration of the baryta, the equation may be written:

$$v = \frac{cqs}{k + q},$$

c being the concentration of the baryta in gramme-equivalents per litre; $s = 0{\cdot}168$ and $k = 26{\cdot}5$.

For hydrolysis by means of nitric acid the values found for these constants were $s = 0{\cdot}000347$ and $k = 3{\cdot}21$. Hence when the proportion of nitro-cellulose to liquid is high, as it is in the boiling vats, hydrolysis is about 480 times as rapid in an alkaline solution as in an acid solution of equal strength. For this reason it is unadvisable to use strong alkalis for the stabilization; caustic alkalis should be avoided and sodium carbonate should only be used when the water otherwise contains no alkali. Hard water possesses sufficient alkali in the form of calcium bicarbonate without any addition, and this is the most suitable for stabilizing nitro-cellulose. Moreover, treatment with

[1] Briggs, *J.S.C.I.*, 1906, p. 626.
[2] *J.S.C.I.*, 1906, p. 624.
[3] *J.C.S.*, 1906, p. 1759.

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strong alkali is liable to convert the nitro-cellulose into unstable decomposition products.

The two methods of stabilization are often combined, that is to say, after the nitro-cotton has been boiled and pulped it is again boiled. The instructions of the U.S. Army Ordnance Department as revised up to April 18, 1908, are, for instance :

U. S. Ordnance method.

" *Nitrating.*—Cellulose of standard quality shall be dried at a temperature not exceeding 110°. When cold this cotton shall be nitrated in mixed nitric and sulphuric acids. After nitrating, the nitro-cellulose shall be washed in water before boiling.

" *Preliminary boiling.*—The nitro-cellulose shall be boiled at least forty hours, and with not less than four changes of water, in tubs so constructed that the nitro-cellulose shall not come in contact with the steam at a temperature greater than 100°. There shall be complete ebullition or boiling over the entire surface of the tubs. No alkali shall be used in this preliminary purification.

" *Pulping.*—The nitro-cellulose shall then be pulped in fresh water, to which shall be added just enough sodium carbonate to preserve a slight alkaline reaction to phenol-phthalein solution ; the process is continued until the material is thoroughly and evenly pulped to a satisfactory degree of fineness, and shows a clean break when a handful is squeezed and broken into parts. During this process the water shall be changed to such an extent as may be necessary to remove the impurities.

" *Poaching.*—After pulping the nitro-cellulose pulp shall be run to the poachers, settled, and the water decanted. The nitro-cellulose shall then be boiled six hours in fresh water, and during this time not more than 10 gallons of carbonate of soda solution for each 2000 lb. dry nitro-cellulose may be added at intervals. This solution shall contain 1 lb. carbonate of soda per gallon. During this and all other boiling in the poachers the pulp shall be thoroughly agitated by mechanical stirrers. After boiling the nitro-cellulose shall be allowed to settle, and the clear water decanted as completely as possible. The tubs shall then be filled with fresh water, boiled two hours, settled, decanted and refilled with fresh water. The boiling shall then be continued for one hour, and this process repeated three times."

This makes a total of twelve hours' boiling with five changes of water, viz. 6, 2, 1, 1, 1, 1. With only the first of these is an addition of soda allowed.

" After boiling the nitro-cellulose shall have ten cold water washes, each washing to consist of agitation by mechanical means for half an hour in a sufficient amount of fresh water, thorough settling and decanting the clear water ; at least 40 per cent. of the total contents of the poacher shall be drawn off. A sample shall then be taken for subjection to the various tests prescribed for nitro-cellulose. Should the nitro-cellulose fail to meet the required heat

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test, it must be boiled again with two changes of water, the time of actual boiling being five hours without the use of alkali, and then it must be given ten cold water washes in the manner prescribed for the regular treatment."

One of the disadvantages of boiling the pulp in iron hollanders is that it may be necessary to add alkali to neutralize the acid formed. It is better to add it in the form of finely divided calcium carbonate (whitening) than sodium carbonate. Another disadvantage is that the water cannot be removed nearly as completely as when the unpulped nitro-cotton is boiled in wooden vats, from which the water can be allowed to drain very thoroughly. If the pulp be allowed to settle in the hollander too long, it forms a dense mass at the bottom, which prevents the rotation of the stirring arms, and it may be necessary to dig it out.

Cellulose nitrites.

Another class of unstable products that may be present in nitro-cellulose is that of the nitrous esters. These are apparently formed in the hydrolysis of nitro-cellulose ; on treatment with dilute alkali or acid the cellulose residue becomes oxidized whilst the acid residue is reduced. The nitrites of cellulose are so unstable, however, that they are never present in a normal product to any considerable extent. Nicolardot and Chertier [1] succeeded in preparing them by the action of nitrous acid on viscose cellulose suspended in dilute nitric acid. A certain amount of nitrate is formed at the same time, but this can be separated from the nitrite by dissolving it in acetone. It can also be made by passing nitrous gases through a mixture of acetic acid and acetic anhydride in which viscose cellulose or ramie fibre is suspended. The products thus prepared are of a grey colour, gelatinous when moist, brittle when dry, insoluble in water, alcohol, ether, acetone, chloroform and ethyl-acetate. The percentage of nitrogen, as determined by Schloesing's method, could not be obtained higher than 2·5 per cent., that is to say, the higher nitrites decomposed before they could be analyzed. In the Lunge nitrometer they gave no evolution. Even those with 2·5 per cent. gradually evolve nitrous fumes at the ordinary temperature, and water and strong acids split the nitrous acid off rapidly, but acetic acid has little effect. It is possibly the presence of these nitrites, which causes unstabilized gun-cotton to give low results when tested in the nitrometer. It is found that on boiling the nitrogen as determined by the nitrometer goes up, whilst that as determined by the Schloesing (Schultze-Tiemann) method goes down. Although nitrites of cellulose are probably formed to some extent in the nitration process, their presence is to be ascribed more to the decomposition of the nitric esters. Their presence must be a cause of instability.

Products of decomposition.

The intermediate products formed in the decomposition of nitro-cellulose have engaged the attention of various investigators, who have hoped to obtain evidence as to the constitution of the cellulose molecule. Thus Kerk-

[1] *C.R.*, 1910, 151, p. 719.

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hoff [1] detected tartaric and citric acids among the products of saponification, and Hadow [2] found oxalic acid and ammonia and an acid similar to saccharic. Divers [3] found in the decomposition products acids which from their reactions he identified as pectic, and para- and meta-pectic acids. Abel [4] confirmed the presence of these in gun-cottons that were badly decomposed; he also found formic and oxalic acids and cyanogen, and when the material was heated with potash, ammonia was given off. Fermentable carbohydrates were only formed in a few instances. Silberrad and Farmer [5] extracted with water 100 kg. of gelatinized nitro-cellulose powder, which had been heated for twenty-three weeks at 54·4°. In the extract they detected ethyl nitrite, ethyl nitrate, ethyl-alcohol (these evidently derived from the alcohol used for the gelatinization), nitric and nitrous acids, ammonia, formic, acetic, butyric, dihydroxy-butyric, oxalic, tartaric, isosaccharinic and hydroxy-pyruvic acids. Carbohydrates were found to be present by the fermentation test, and some other compounds were obtained, but could not be identified by reason of the complexity of the mixture and their minute quantity. Hydroxy-pyruvic acid, $C_3H_4O_4$, has also been found by Will [6] and Vignon [7] among the products of the alkaline saponification of nitro-cellulose and nitro-oxy-cellulose respectively. Berl and Smith [8] obtained it (called by them oxy-pyruvic acid) by the alkaline hydrolysis not only of nitro-cellulose but also of the nitrates of glucose and levulose, showing the intimate relationship of cellulose with these other carbohydrates. From starch nitrate a similar but not identical acid was obtained. They also found that hydroxy-pyruvic acid is very susceptible to oxidation and fermentation, and consequently may be the substance which others have described as "fermentable carbohydrates." Berl and Fodor [9] found that the relative proportions of the different acids formed vary according to the concentration of the alkali used, a dilute solution yielding compounds containing 4 to 5 carbon atoms, whilst with concentrated alkali acids with 1 to 3 carbon atoms predominated. In addition to hydroxy-pyruvic acid they detected malic, trihydroxy-glutaric, malonic, tartronic, oxalic, glycollic and dihydroxy-butyric acids.

Berl and Fodor [10] have also examined the nitrogenous residues left on treatment with alkali. A solution of collodion cotton was shaken for several weeks with a dilute solution of sodium carbonate. At the surface between the two liquids a flocculent substance separated out, which was found to contain 8·4 per cent. nitrate nitrogen as determined by the nitrometer, and 9·0 per cent. total N by the Dumas method. The same substance was separated

[1] *J. f. prakt. C.*, 1847, p. 284.
[2] *J.C.S.*, 1854, p. 201.
[3] *J.C.S.*, 1863, p. 91.
[4] *Phil. Trans.*, 1867, p. 181.
[5] *J.C.S*, 1906, p. 1182.
[6] *Ber.*, 1891, pp. 400, 3831.
[7] *C.R.*, 1907, p. 872.
[8] *J.S.C.I.*, 1908, p. 534.
[9] *S.S.*, 1910, pp. 296, 313.
[10] *S.S.*, 1910, pp. 254, 269.

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from the ether-alcohol solution after the unchanged nitro-cellulose had been removed by precipitation with water. When the aqueous liquid thus obtained was acidified a precipitate was obtained (also a slight smell of prussic acid), and this was purified by dissolving in 96 per cent. alcohol and reprecipitating with water. The action of caustic potash on collodion cotton in solution also yielded the same substance. It was soluble in alcohol but insoluble in ether ; on analysis it gave results agreeing with the formula $C_{24}H_{33}O_{21}(NO_2)_5$, and may therefore be considered as a pentanitro-oxy-cellulose. It differed from normal penta-nitro-cellulose in having two hydrogen atoms replaced by one oxygen. Its solutions showed little viscosity, and molecular weight determinations gave results agreeing fairly well with the formula. The authors gave the substance the name " cellonic acid nitrate." Besides this another substance was obtained, which was soluble in ether. This was considered to be cellonic acid nitrite. The cellonic acid nitrate was not very stable ; it exploded at 163°.

Will and Lenze [1] considered that the instability of some samples of nitro-cellulose may be due to the formation of sugars from the cellulose, and the conversion of these into nitrates. They accordingly prepared and examined various nitrates of the carbohydrates (*see* next chapter), which they found to be all more or less unstable. Sugar nitrate cannot be formed in the nitration of cellulose, however, unless the sugar be present beforehand, as the nitration is a much more rapid reaction than the formation of sugar from cellulose, and although sugars are apparently formed sometimes in the decomposition of nitro-cellulose, they are among the products of the ultimate breaking down of the material, and they are no longer nitrated. The presence of these foreign carbo-hydrates should be excluded from the cellulose used for nitration ; starch is the one that is most likely to occur.

Washing collodion cotton.

Collodion cotton for the manufacture of blasting gelatine is not boiled, because the power of forming a stiff colloid would thereby be much reduced. It is washed repeatedly with hot water slightly below the boiling-point.

[1] *Ber.*, 1898, p. 68.

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CHAPTER XIV

NITRIC ESTERS OF OTHER CARBOHYDRATES

Nitro-starch : Nitro-sugars

Nitro-starch. NITRO-STARCH has been known even longer than nitro-cotton, for it was first prepared by Braconnot in 1833 [1] by dissolving starch in strong nitric acid and pouring the viscous translucent liquid into water. The resulting cheesy white substance was called by him " xyloidine," a name which is now applied generally to any product that is made by dissolving a carbo-hydrate in nitric acid and pouring into water or sulphuric acid, or by dissolving in sulphuric acid and pouring into nitric. Nitro-starch was afterwards investigated by Pélouse,[2] Liebig, Buijs-Ballot, Gerhard, Béchamp,[3] and Reichardt. In spite of the cheapness of the raw material, starch, it has never been able to displace nitro-cotton ; this is partly due to the instability of nitro-starch, and partly to the mechanical difficulties in nitrating and purifying it. If the starch be introduced into the mixed acids in the same way that cotton is, it forms clots, which are not thoroughly acted upon, and are difficult to purify subsequently. Hence in all the early attempts to manufacture the substance the starch was dissolved in nitric acid and poured into sulphuric acid. Such, for instance, was the method of the Austrian engineer officer Uchatius.[4] The process of the Viennese Nobel Company [5] consisted in dissolving ground starch in nitric acid (specific gravity 1·501), and then injecting it as a spray into the waste acids from nitro-glycerine (HNO_3 10 per cent., H_2SO_4 70 per cent., H_2O 20 per cent.), the temperature being kept down to 20° to 25°. The nitro-starch was then filtered off on a filter of gun-cotton, washed with water and treated for twenty-four hours with 5 per cent. soda. It was then ground to a paste and washed in a centrifugal or filter-press and impregnated with aniline with the object of making it stable. Until it was required for further use it was kept wet, containing about 33 per cent. water and 1 per cent. aniline.

[1] *Ann. chim. phys.*, 52, p. 290.
[2] *Ann. pharm.*, 1839, (29), p. 38 ; *C.R.*, 23, p. 893.
[3] *Ann. chim. phys.*, 1862, p. 311.
[4] *Dingler's poly. Journ.*, 1861, p. 146.
[5] Germ. Pat. 57,711.

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Hough's process [1] differs from previous ones in that he injects powdered starch by means of a jet of air into mixed acid containing an excess of sulphuric anhydride, which excess is maintained during nitration by the addition of more oleum. The nitrated product is filtered off and treated with hot ammonia. He claimed thus to obtain a stable product containing about 16·5 per cent. N. These claims have been investigated by Berl and Bütler,[2] only they did not treat the product with alkali, as this could only have an injurious effect on the stability: they treated it with water only. They found that the products were very unstable, the heat tests low, as also the ignition points, and they contained 0·50 per cent. combined sulphuric acid. The percentage of nitrogen also was very much lower than as stated by Hough; in no case was it more than about 13·4 per cent., which was the same as nitro-cotton contained when it was nitrated in the same manner.

The Nobel and other methods were similarly investigated by Mühlhäuser.[3] The principal results are collected together in the following Table:

Method of Preparation	Per cent. N.	Solubility in		Ignition Point	Remarks
		Alcohol	Ether-Alcohol		
Pptd. with N/G waste acid . .	11·02	sol.	sol.	175°	M, Nobel process
,, water . . .	10·54	,,	,,	170°	M.
,, 3·5 pts. H_2SO_4 . .	12·50	insol.	,,	121°	M.
,, 3 ,, . .	12·87	,,	,,	152°	M.
,, 3 ,, . .	13·32	,,	,,	155°	M.
Injection. Wheat starch . .	13·23	,,	dif. sol.	121°	B, Hough process.
,, Potato ,, . .	13·44	,,	,,	120°	B, ,, ,,
,, Rice ,, . .	12·86	,,	sol.	135°	B, ,, ,,
,, Soluble ,, . .	13·35	,,	,,	120°	B, ,, ,,

M means investigated by Mühlhäusen; B by Berl and Bütler.

None of these were stable except the first two, which contained only 11 and 10·5 per cent. N respectively, but, on the other hand, Will and Lenze,[4] by treatment with solvents, obtained a stable product with 14·04 per cent. N. To prepare this they dissolved the dried starch in concentrated nitric acid (specific gravity 1·52), which was kept cool, and after twenty-four hours sulphuric acid was gradually added. The product was washed with water, then extracted first with cold alcohol and afterwards twice with hot alcohol. It was

[1] U.S. Pats. 751,076 of February 2, 1904 and 790,840 of May 23, 1905.
[2] *S.S.*, 1910, p. 82. [3] *Dingler's Polyt. Jour.*, 1892 (284,), p. 37. [4] *Ber.*, 1898, p. 68.

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dissolved in a mixture of acetone and alcohol and the acetone evaporated off, thereby precipitating the nitrate as a white powder. This was then boiled with alcohol, washed with water and dried. The product purified in this way ignited only at 194°, and after keeping at 50° for six months was still quite stable. Such a process is, of course, quite unsuitable for use on a commercial scale, but it seems to indicate that nitro-starch itself is fairy stable if it can be separated from impurities.

Nitro-starch dissolves readily in acetone and ethyl-acetate. The solubilities in alcohol and ether-alcohol are given in the above Table. That made by the Nobel process dissolves very readily in nitro-glycerine, but does not gelatinize it as collodion cotton does. This is in accordance with the low viscosity of the solutions in acetone. Berl and Bütler obtained the following viscosities for solutions of potato starch nitrated by Hough's method and for nitro-cellulose nitrated in the same way, both containing 13·4 per cent. N.

	1 per cent. solution	2 per cent. solution	5 per cent. solution
Potato starch nitrate	1·74	2·66	9·47
Cellulose nitrate	95·1	1,005	85,640

Acetone = 1

Other varieties of starch gave even lower viscosities. The molecular complexity is in fact small; Saposhnikoff [1] determined the molecular weight in a Beckmann apparatus with boiling acetone for two different products each containing 13·4 per cent. N, and obtained results agreeing with a C_{36} formula.

One of the disadvantages of nitro-starch as compared with nitro-cotton lies in the fact that it absorbs a much larger amount of moisture from the air, just as starch is more hygroscopic than its homologue, cellulose. Thus Will [2] found that the materials after being dried in an oven at 40° took up the following amounts in an atmosphere nearly saturated with moisture at 25°:

	Hygroscopicity (per cent.)
Cotton	7 to 8
Wheat starch	11·4
Maize ,,	10·6
Potato ,,	14·1
Rice ,,	11·4
Soluble ,,	11·3

and the corresponding figures for the nitrated products were found by Will and Berl and Bütler to be:

[1] *J. Russ. Phys. Chem. Soc.*, 1903, p. 126; *J.C.S.* Abs., 1903, p. 402.
[2] *Mitt. a.d. Centralstelle*, No. 4.

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	Per cent. N	Hygroscopicity	Hygroscopicity of nitro-cotton with same per-centage N°
Rice starch nitrate (W) . . .	8·51	7·37	6·1
Soluble „ „ (W) . . .	12·95	8·40	1·6
Potato „ „ (B) . . .	13·44	6·57	1·2

Nitro-starch has never come into general use in Europe, principally because of its unsatisfactory stability, in spite of the efforts of Uchatius and the Austrian Nobel Company to make smokeless powders with it. It is not authorized for manufacture or importation into England. In America, however, it is used as a component of high explosives.

Nitro-sugars. By the action of nitric acid on various sugars products can be obtained containing 16 to 17 per cent. N. They can be exploded by friction and go off with great violence. Attempts have therefore been made to use them for percussion-caps, but they have hitherto proved too sensitive, too hygroscopic, and too liable to spontaneous decomposition. A number of these substances were prepared and examined by Will and Lenze.[1] The general method of preparation was to dissolve the sugar in nitric acid, add sulphuric acid, separate, wash with ice water, and purify by recrystallization from alcohol. The following Table gives the principal results :

	Melting-point	Per cent. N	Loss at 50°	Decom-poses at
MONOSACCHARIDES—				
Pentoses, $C_5H_{10}O_5$:				
Ramnose tetranitrate . . .	135°	16·08	1·2% in 30 days	—
Arabinose „ . . .	85°	16.75	1·5% in 1 day 40% in 40 days	120°
Xylose „ . . .	141°	14·57	—	—
Hexoses, $C_6H_{12}O_6$ Aldoses :				
Glucose pentanitrate . . .	10°	16·96	38% in 1 day	135°
Galactose „ . . α	115°–116°	17·18	42% in 10 days	126°
„ „ . . β	72°–73°	17·08	42% in 1 day	125°
Rhamnose „ . . .	81°–82°	17	46% in 1 day.	124°
Ketoses :				
Levulose trinitrate . . α	137°–139°	14·12	0 in 180 days.	145°
„ „ . . β	48°–52°	13·83	1–3% in 8 days	135°
Sorbinose „ . . .	40°–45°	14·04	—	—

[1] *Ber.*, 1898, pp. 68–90.

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	Melting-point	Per cent. N	Loss at 50°	Decomposes at
MONOSACCHARIDES—(*continued*)				
Heptoses, $C_7H_{14}O_7$:				
Glucoheptose hexanitrate	100°	17·39	—	—
Glucosides:				
α-Methylglucoside tetranitrate	49°–50°	15·14	0·7% in 5 days	135°
α-Methyl-d-mannoside tetranitrate	36°	15	—	—
BISACCHARIDES, $C_{12}H_{22}O_{11}$—				
Cane sugar octonitrate	28°–29°	15·79	11% in 3 days	135°
Lactose ,,	145°–146°	15·48 16·40	0·7% in 8 days 40% in 40 days	135°
Maltose ,,	163°–164°	15·83	1·3% in 11 days 23% in 43 days	163°–4°
Trehalose ,,	124°	16·11	—	136°
TRISACCHARIDES, $C_{18}H_{32}O_{11}$—				
Rafinose endekanitrate	55°–65°	15·39	—	136°

The product from levulose appears to be the most stable; those from maltose and lactose also did not decompose very readily.

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PART V

NITRIC ESTERS OF GLYCERINE

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CHAPTER XV

GLYCERINE

Source of glycerine : Soap boiling : Purification of spent lye : Concentration : Autoclave process : Combined process : Twitchell process : Ferment process : Distillation

GLYCERINE, $C_3H_8O_3$, is a by-product in the manufacture of soap and stearine candles from oils and fats, which consist almost entirely of the glycerides of the fatty acids compounds formed by combining three molecules of a fatty acid, stearic acid for instance, $C_{17}H_{35}CO_2H$, with one of glycerine and eliminating three molecules of water. When the oils or fats are heated with solutions of caustic alkalis or acids, or even with water alone the glyceride is split up : **Source of Glycerine.**

$$\underset{\text{Water}}{3H_2O} + \underset{\text{Tristearine}}{C_3H_5(C_{17}H_{35}CO_2)_3} = \underset{\text{Glycerine}}{C_3H_5(OH)_3} + \underset{\text{Stearic acid}}{3C_{17}H_{35}CO_2H}$$

If caustic soda has been used, it combines with the acid to form a soap such as sodium stearate, $C_{17}H_{35}CO_2Na$. Stearine candles, on the other hand, are made from the free fatty acid and principally from stearic and palmitic acids.

The soap industry is, of course, a very old one, but it is only in modern times that the recognition of the advantages of cleanliness has caused it to assume really large dimensions. Formerly the glycerine was either left in the finished soap, or was allowed to run to waste. It is only since the development of the industry of nitro-glycerine explosives that there has been a large demand for the product. Since the end of the Boer War in 1902 the gold-mines in South Africa have developed considerably, and in consequence of the improvements in metallurgy it now pays to extract gold from much poorer ores. The result is that in 1907 the consumption of explosives in South Africa was twice as great as before the war. But from the end of 1907 until July 1908, the financial crisis in the United States put a stop to all great engineering works there. Since then, however, there has been a great increase in consumption ; and the Panama Canal works alone have taken some millions of pounds of nitro-glycerine explosives. The result has been a great rise in the price of glycerine : whereas in January 1906, crude 80 per cent. was quoted at £28 per ton, and commercial distilled (specific gravity 1·260) at £55, the prices now (1914) are £55 to £65 and £90 to £100 respectively. It now pays the soap-maker to recover a much larger proportion of the glycerine than formerly.

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Soap boiling. The simplest method of making soap is to boil the oil with caustic soda solution in open tanks (" kettles "), which usually hold 40 to 50 tons. The saponification is started with a weak lye of specific gravity 1·05 (4·6 per cent. NaOH), and when the action is well started stronger lyes are added. When the action is almost complete, salt is added to render the soap insoluble in the water. Two layers are thus obtained : an upper one of soap, and a lower one of brine containing the glycerine dissolved in it. The soap is separated, the saponification is completed by the addition of a little more soda, and it is submitted to such further processes as are necessary to produce the class of soap required.

There are a number of other processes of splitting up the fats with separation of the fatty acids as such, and these acids can subsequently be combined with soda to form soaps. These methods have been used largely in Germany for soap-making, but the manufacture of soap is thus rendered much more difficult ; the soap is often dark in colour, and is apt to " grain " on keeping, and in many cases becomes rancid. These disadvantages more than compensate for the fact that the recovery of the glycerine is easier. In England saponification with soda is practically universal, and it is the process most used in America. The tendency in Germany is also to return to this method for the manufacture of soap.

Purification of spent lye. The spent lye contains, besides glycerine and much water, a large amount of sodium chloride, and various impurities, organic and inorganic. It is first necessary to remove some of the impurities. The free alkali is first neutralized with sulphuric or hydrochloric acid, and if impure soda has been used, ferric or aluminium chloride is added as long as a precipitate is formed to free the liquid from hypo-sulphites, sulphides, cyanides, sulpho-cyanides, etc. The precipitate, which is allowed to settle, contains Prussian blue and fatty matters, which are recovered. Other methods of purification are also adopted according to the composition of the lye.

Concentration. The next step is to concentrate the lye. During this operation considerable quantities of salt separate and cause trouble by coating the solid surfaces and preventing the transmission of heat. Various types of plant have been devised for carrying out this operation, such as that of L. Droux, of Paris, consisting of a steam-heated drum revolving in a shallow tank filled with the liquid ; the removal of the salt is easy with a plant of this kind. At the present time the concentration is usually carried out in single or multiple effect vacuum evaporators, in which the liquid is kept circulating rapidly, so that solid deposits may not be formed on the heating surfaces.

If the fatty acids are to be used for the manufacture of candles, other processes of treating the oil or fat can be used, as the acids have to be distilled *in vacuo* in any case, in order to remove the dark-coloured impurities. It is also necessary to remove from them oleic acid, which has a melting-point of

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only 14° and would consequently make the material too soft; the melting-points of stearic and palmitic acids are 48° and 62° respectively. This is effected partly by filtration and partly by distillation.

The method, which was first used for the manufacture of stearine was to saponify with an excess of milk of lime, separate the glycerine from the lime soap, and decompose the latter with sulphuric acid. The consumption of lime and sulphuric acid was considerable, however, and the process was troublesome. Then it was found that a much smaller proportion of lime would suffice, if the operation were carried out at a high temperature and pressure. The treatment is effected at a pressure of about 120 lb. per square inch in an autoclave, provided with a mechanism for stirring. A little zinc oxide is also added sometimes to hasten the reaction. According to Lewkowitsch [1] the yield of "saponification crude glycerine" of specific gravity 1·240 by this process is about 10 per cent.

Autoclave process.

It is possible to do away with the lime entirely, and resolve the fat into acids and glycerine by merely heating with water in an autoclave, but the temperature required is high and the time long, and consequently there is much decomposition, with the result that the yields are bad and the products impure. But instead of alkaline substances such as caustic soda and lime, many other materials may be used to accelerate the saponification. One of these is sulphuric acid, which is much used for the production of candle stearine. The fat is heated to about 120° and mixed intimately with 4 to 6 per cent. of C.O.V. The yield of glycerine by this process is only 8 or 9 per cent.; the acids are very dark in colour, but a large yield is obtained of material suitable for candle making, 61 to 63 per cent. as against 45 to 47 per cent. by the autoclave process. This is due to the action of the sulphuric acid upon the oleic acid, which is converted into iso-oleic and hydroxy-stearic acids, stearo-lactone and other bodies having comparatively high melting-points. Unfortunately some of these are broken down again in the subsequent distillation.

Combined process.

The advantages of both processes can be combined by first heating in an autoclave with a small proportion of lime, and subsequently treating the fatty acids with concentrated sulphuric acid. According to Lewkowitsch [2] the yields from 100 parts tallow are then:

Candle material	61–63 arts
Oleic acid	30–32 ,,
Crude glycerine (s.g. 1·240)	10 ,,
Pitch and loss	2–3 ,,

Twitchell process.

In the Twitchell process [3] the fat is treated with a reagent made by the action of sulphuric acid on oleic acid dissolved in an aromatic hydro-carbon,

[1] *Oils, Fats and Waxes*, 4th ed., vol. iii., p. 178. [2] *Loc. cit.*, p. 188.
[3] Am. Pat., 601, 603, March 29, 1898.

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such as naphthalene. This reagent greatly accelerates the hydrolysis of the fat, but it is not known how it acts. The fat mixed with ½ to 1 per cent. of the reagent and some water is boiled for twelve to twenty-four hours with live steam in a tank closed to prevent access of air, which would make the acids dark. The fatty layer now contains 85 to 90 per cent. of free fatty acids. The contents of the tank are allowed to settle, and the aqueous layer containing the glycerine is drawn off. A small quantity of water is then added, and the boiling is continued for another twelve to twenty-four hours. The conversion is then 97 to 98 per cent. Barium carbonate is then added until the water is neutral to methyl orange, as the presence of strong acids causes the material to discolour. This process is much used in America for the manufacture of candle material.

Ferment process.

Another catalytic agent that is used to accelerate the saponification of fats is the enzyme contained in castor-oil seeds. The reagent is prepared by decorticating the seeds, grinding them up with water, and allowing them to ferment. A creamy emulsion rises to the surface containing some 4 per cent. of albumenoid substances, which constitute the active agent. The oil to be saponified is mixed with about 40 per cent. of water and stirred to an emulsion by means of air, 5 to 8 per cent. of "ferment" are added, and 0·2 per cent. of manganese sulphate, which greatly assists the action. The whole mass is kept at a suitable temperature, which should not be above 35°, but must, of course, be higher than the melting-point of the fat. In the case of fat of high melting-point it is necessary to mix it with oil. The fermentation is allowed to proceed for one or two days, and if the emulsion shows signs of settling out, it is stirred up again with air. It is not practicable to attain much more than 80 per cent. conversion by this process. When it is finished a little sulphuric acid is added to cause the emulsion to separate, and the temperature is raised to about 80° to destroy the enzymes. Some difficulty is caused by the slowness with which the emulsion separates out; the incompleteness of the conversion is also an objection. The advantages of this and the Twitchell process are that the plant required is very simple and inexpensive, and the colour of the acids is good. The losses by either may be heavy, however, if they are mishandled.

Distillation.

Glycerine that is to be used for the manufacture of nitro-glycerine has to be purified by distillation. At one time the distillation was carried out at atmospheric pressure with superheated steam in a still heated by a fire. Under these conditions much of the glycerine was decomposed and polyglycerines were formed. Distillation with saturated steam *in vacuo* did not give good results, because the temperature of the steam was reduced too much by the expansion. The distillation is now generally carried out with superheated steam *in vacuo*. There is no great difficulty in separating the glycerine from the water in the distillate, as the boiling-points are very far

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apart (290° and 100° respectively at atmospheric pressure), but the distillation must be carried out with proper care to obtain the glycerine in a satisfactory state of purity. The glycerine is generally condensed in a series of metal pipes cooled by exposure to the air. In the first tubes practically anhydrous glycerine condenses; in the later ones the condensate is somewhat dilute. The former only is used for the manufacture of nitro-glycerine, the latter for a variety of purposes, such as filling gas-meters, the manufacture of ink and

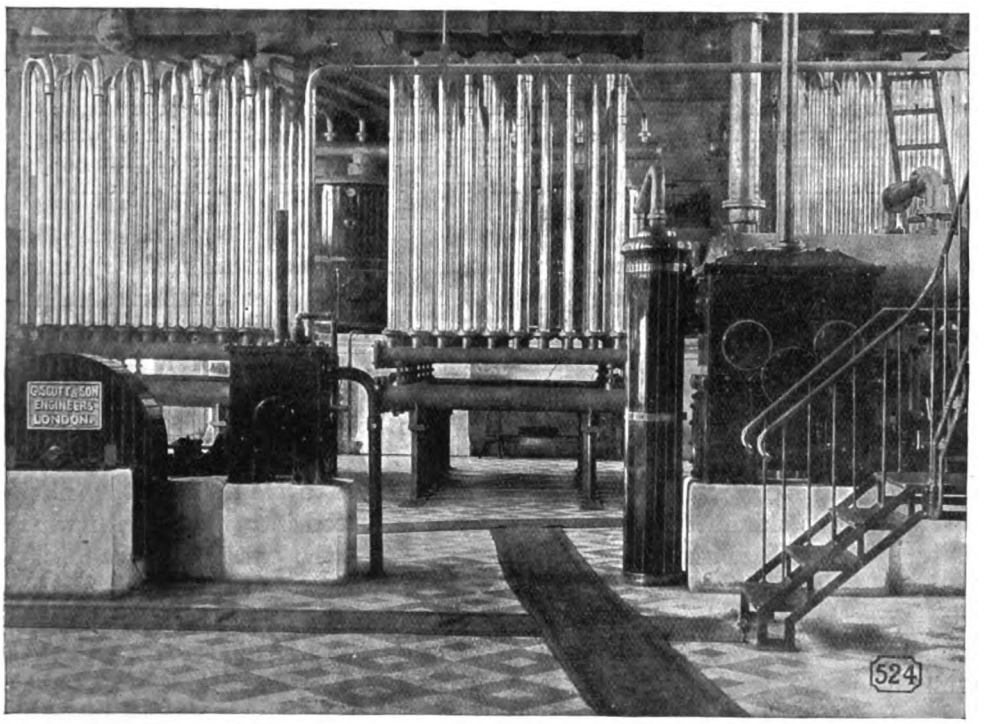

FIG. 36. Distillation Plant for Glycerine

sizes for textiles. Fig. 36 shows a distillation plant of the type made by George Scott and Sons, London, and very largely used in England. Over the vertical still shown in the background is a catch-pot, in which high boiling impurities, such as poly-glycerines are condensed, and material such as salt, that is carried along mechanically by the vapours, is held back. After passing through the air-cooled battery, shown in the foreground, in which the glycerine is condensed, the vapour passes to a condenser cooled with water, where the water is condensed, and then to a vacuum pump. The cost of distillation is stated to be about £1 per ton.

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CHAPTER XVI

MANUFACTURE OF NITRO-GLYCERINE

Early methods : Injector : Modern plant : Nitrator : Separator : Pre-wash tank : Washing : Filtering : Wash-waters : After-separation : Recent improvements : Abolition of cocks : Fume hoods : Plugs for air-holes : Softening the washing waters : Washing operations : Labyrinths : Nitrator-separator : Cooling coils : Prevention of after-separation : Drowning arrangements : Acids and yields : Time of separation : Conveyance of nitro-glycerine : Gutters : Location of factory : Air-supply : Limit boards : Thunder-storms : General precautions

Early methods.

In the early days nitro-glycerine was made on quite a small scale by hand. The mixed acids were placed in a pot of iron, lead, or earthenware, surrounded by a trough containing cold water. The glycerine was then poured in slowly while the liquid was stirred by means of a rod of iron or glass. The yield obtained was sometimes as much as 2 lb. of nitro-glycerine from 1 lb. of glycerine, but was frequently considerably less. After all the glycerine had been added, the stirring was continued for a few minutes longer, then the liquid was allowed to stand and the nitro-glycerine was skimmed from the surface and poured into water, with which it was agitated. Finally it was separated from the water by means of a separating funnel. With the development of the dynamite industry the demand for nitro-glycerine grew enormously, and mechanical appliances were gradually introduced to enable larger quantities to be dealt with at a time, thus saving labour and improving the yield. Descriptions of these are to be found in the older text-books, such as those of Guttmann and Chalon.

A few years after the discovery of dynamite by Nobel in 1866 most of the essential features of the modern plant had been introduced. The nitrating vessel was a large cylindrical leaden tank with an outer wooden casing, forming a jacket through which cold water was circulated.[1] In the tank there were also coils through which cold water ran. Agitation was effected by means of compressed air led in through lead pipes, and in the earlier plants mechanical agitation was also employed. The glycerine was run in from a tank placed above the nitrator through a cock by means of which the inflow was controlled. The fumes passed away through a glass pipe, which enabled the man in charge to observe their colour. He also watched the temperature

[1] *See* Nathan and Rintoul, *J.S.C.I.*, 1908, p. 194.

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by means of a long thermometer, the scale of which was above the cover, whilst the bulb was in the acid mixture. Below the nitrator a large tank was provided containing water into which the charge could be run if the temperature rose beyond control. On completion of the nitration the whole of the charge of waste acids and nitro-glycerine was run slowly into a large tank of water, which was kept in agitation by means of wooden paddles operated by hand or mechanically. The nitro-glycerine was allowed to separate out at the bottom of this tank, and was then drawn off into smaller vats and washed several times with soda solution and water until neutral.

This system involved the loss of the whole of the waste acids, and if the rate of flow into the water was not controlled very carefully, a dangerous amount of heating was liable to occur. In any case much nitrous fume was formed and there was some loss of nitro-glycerine through decomposition. For these reasons the separating tank was introduced towards the end of the 'seventies. The charge was run into this through a cock at the bottom of the nitrator, and the nitro-glycerine being lighter than the acids separated out at the top, and was transferred to the washing tank.

Modern plant.

In America iron nitrators are still used. These have double walls, within which cold water circulates, and are provided with mechanical agitators instead of, or in addition to, compressed air. In Europe, however, such plant has long ago been superseded by leaden vessels in which the liquids are agitated by jets of air. The water before being passed through the coils is generally cooled by means of refrigerating plant to a temperature only a few degrees above its freezing-point. This enables the nitration to be carried out more rapidly and at a lower temperature. The outer water jacket has been done away with. The nitrator has frequently been made in the form of a wooden tank lined with lead, but the best modern practice is to construct it of lead only, sheet being used of sufficient thickness to stand without support.

Nitrator.

The form that the nitro-glycerine plant had generally assumed by the end of the nineteenth century may be seen from the diagram of the factory that was erected at Waltham Abbey in 1890 (Fig. 37). The nitrator was of the form that has just been described. The top consisted of a dome of lead, which was cemented on and provided with glass inspection windows. The air pipes, the pipe for the mixed acids, and the inlet and outlet pipes for the cold water coils all passed through holes in the cover; in the centre of the cover was a man-lid with an acid lute, and in the centre of that again was a hole for the insertion of the glycerine injector. This hole was closed by a loose lead plug when the injector was removed. The air used for the agitation was allowed to escape through a fume-pipe fitted with a glass cylinder to enable the man in charge to observe whether red fumes were being developed. The bottom of the tank was provided with two earthenware cocks, both of which

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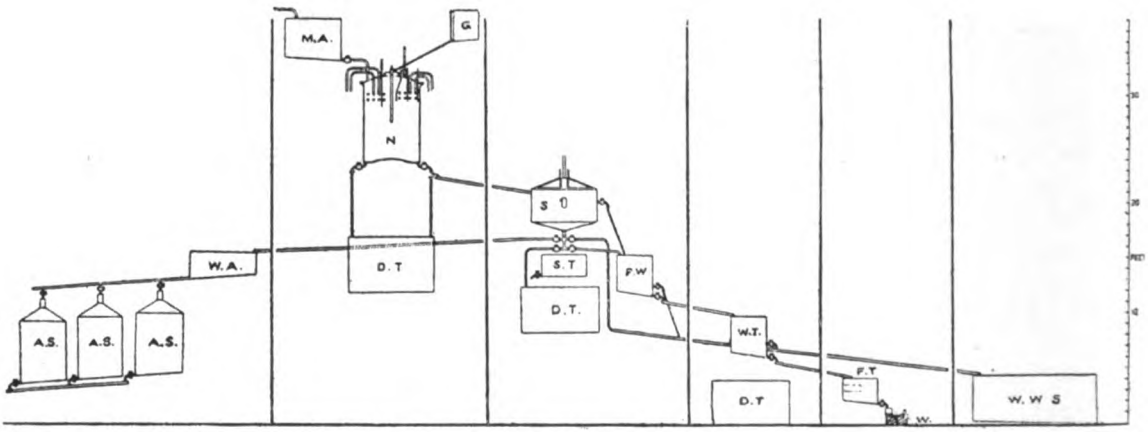
were available if it should be necessary to drown the charge ; one of them was used for running the contents of the nitrator into the separating tank through a movable lead bend.

The mixed acids having been run into the nitrator the glycerine injector was introduced through the hole in the man-lid, and the glycerine was sprayed by means of air pressure under the surface of the acid. During nitration cold water was passed through the coils, and the contents of the nitrator were kept in a state of violent agitation by means of numerous jets of compressed air. The inflow of glycerine was regulated so as to keep the temperature of the charge at or below 22° C. When all the glycerine had been added, the injector was removed, the charge cooled down to about 15°, and then run



After separating house | Nitrating house | Separating house | Washing house | Weighing and mixing house | Wash water settling house

W.A. Waste acid tank.
A.S. After separating bottles.

M.A. Mixed acid tank.
G. Glycerine tank.
N. Nitrator.
D.T. Drowning tank.

S. Separator.
S.T. Safety tank.
D.T. Drowning tank.
P.W. Pre-wash tank.

W.T. Washing tank.
D.T. Drowning tank.

F.T. Filter tank.
W. Scales.

W.W.S. Wash water settling tank.

FIG. 37. Diagram of Old Nitro-glycerine Plant at Waltham Abbey

off into the separator. In factories where refrigerated water is not available it is not always possible to nitrate at such a low temperature : the German official regulations lay down that the temperature shall never exceed 30°, and the charge must not be run into the separator until it has been reduced to 25°.

Injector. For introducing the glycerine into the acids an ingenious form of injector was used by Nobel, and was adopted in many factories. It consists of two metal tubes one within the other ; the outer one is for the glycerine, and the inner one for compressed air, and there are two flexible diaphragms so arranged that if the air pressure fail, or if it rise too high, the supply of glycerine is cut

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off. The air carries the glycerine in the form of a fine spray into the mixed acids. Formerly this appliance was made of iron, but it is now generally built of aluminium. Its one disadvantage is that it requires constant attention to keep it in good working order, and for this reason many prefer to use a simpler appliance consisting merely of a rose of lead or aluminium having a large number of holes. Through this the glycerine is forced from a closed tank by means of air pressure, and falls as a fine rain on the surface of the acid, with which the globules are caused to mix at once by the violent agitation.

Separator.

At Waltham Abbey the separator was situated in the same building as the nitrator and the preliminary washing tank, but in many other factories the nitrator is in a building by itself, and the separator and preliminary washing tank in another. The separator at Waltham Abbey was a square lead tank, the bottom of which sloped down from all four sides to a central hole fitted with a vertical glass cylinder. A horizontal lead pipe with branches in four directions was connected to the lower end of the cylinder, and each branch was provided with an earthenware cock. Under the separator was a lead-lined tank for the purpose of catching the contents of the separator in case the glass cylinder should break. The separator was provided with a skeleton frame cover filled in with glass, the sides sloping up to a pipe which carried off the fumes; air pipes were led into the separator through the cover, so that if there should be any sign of spontaneous heating in the nitro-glycerine, it could be stirred up and mixed again with the waste acids, which would reduce the temperature once more. A thermometer passed through the lid of the vessel with its bulb in the nitro-glycerine and its scale above the lid, so that any rise of temperature could be seen at once. On the side of the separator there was a glass inspection window, also an earthenware cock situated about 4 inches below the surface of the nitro-glycerine. When the separation was complete, the bulk of the nitro-glycerine was run off through this cock into the preliminary washing tank. The waste acid was then run away through one of the branches of the bottom pipe to the "after-separating house." As soon as the rest of the nitro-glycerine was seen coming down into the glass cylinder, the cock leading to the after-separating house was closed, and the one leading to the "pre-wash" tank was opened, and the remainder of the nitro-glycerine run into this tank. Of the other two cocks at the bottom of the separator one was used for running to the "wash-water settling house" any thick sludge, that separated at the surface dividing the acid from the nitro-glycerine, and the other was connected to the drowning tank.

In some factories an open separator was used instead of a closed tank, and the nitro-glycerine as it separated was removed by hand with a metal skimmer, generally of aluminium, and transferred little by little to the pre-wash tank.

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Pre-wash tank. The old pattern of preliminary washing tank, usually called the "pre-wash tank," was fitted with two earthenware cocks, an upper one for running off the washing waters, and the lower one to run the nitro-glycerine to the washing house. The air pipe for agitating the charge was laid loosely on the bottom; another pipe was led into the bottom faucet down the inside of the tank; the tank was open at the top. The object of "pre-washing" is to remove the bulk of the acid from the nitro-glycerine as quickly as possible, and render it almost neutral before it is sent down to the washing house. To do this it is agitated for a few minutes with about four different lots of wash-water and then with a weak solution of sodium carbonate.

Washing. The washing tank was similar to this and was provided with cocks, one at the bottom for running off the nitro-glycerine, and one or more skimming cocks at different levels. An alternative arrangement for running off the wash-water was a skimmer, a saucer-shaped funnel attached to a rubber pipe, which led through the side of the tank to the wash-water gutter. The early form of skimmer was of lead supported by means of a rope and counter weight. Later patterns were made of lighter material, such as brass covered with rubber cloth.

Filtering. The filtration of the washed nitro-glycerine is generally carried out in the washing house in a leaden tank. Formerly it was filtered through dry, coarse-grained salt contained in a flannel bag supported on wire gauze. The greater part of the water in suspension in the nitro-glycerine was absorbed by the salt, whilst the nitro-glycerine flowed into the tank. This had an earthenware cock by means of which the nitro-glycerine was run into a rubber bucket standing on the pan of a pair of scales, so that the correct quantity could be weighed out for a charge of the explosive that was to be made. At the end of the day's work, or oftener if necessary, the salt bag was renewed, and the salt was dissolved in warm water to recover any nitro-glycerine it might contain.

The filtration is now carried out at Waltham Abbey not in the washing but in the mixing houses. The nitro-glycerine runs down a gutter to the mixing house, and from there into a plain lead tank with a false bottom of perforated lead, on which lies a layer of sponges sewn up in flannel. The nitro-glycerine filters through the sponges, which retain the moisture and flocculent matter. The nitro-glycerine is drawn off from the tank by means of a rubber tube, through which it flows to the measuring vessel (*see* p. 237) which is placed just below it.

Wash-waters. All the waters used for washing the nitro-glycerine and plant are run down lead gutters into a large tank in the "wash-water settling house," and the contents of the tank are kept agitated by means of compressed air. At the end of the day's work the air is shut off and any nitro-glycerine is allowed to settle out. This is drawn off from the bottom of the tank and returned

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to the pre-wash tank. The residual mud consists mostly of lead sulphate mixed with water and nitro-glycerine and some sand, wool, etc. It is rendered alkaline with soda solution, and filtered and washed with warm water in the "mud hut." This converts most of the lead sulphate into carbonate, and renders the material much less dangerous. The mud is subsequently wrung out in flannel to remove as much nitro-glycerine as possible, and finally it is mixed with kerosine and burnt. At Waltham Abbey the wash-waters are finally run into a small pond, in which a couple of dynamite cartridges are exploded every week so as to destroy any nitro-glycerine that may still be present.

After-separation.

The waste acid from the separator carries with it some nitro-glycerine, which is present in it in three forms: there are some minute globules, which have not had time to separate out completely, there is some in solution in the acids, and there is some, which may be called "potential nitro-glycerine," which has not actually been formed, but is present as mono- and di-nitro-glycerine, and may be converted into tri-nitro-glycerine on standing, so causing a further separation at the surface of the acids. In order to avoid the great danger that would be caused by the separation of nitro-glycerine in any part of the acid plant, the waste acid is generally allowed to stand first for several days in an "after-separator" (German: "Nachscheider"). This consists of a large cylindrical lead tank with a conical top surmounted by a glass cylinder. It is filled until the surface of the liquid is visible inside the glass. Any nitro-glycerine that separates is removed by the attendant with a small aluminium scoop, and washed with water in a small lead tank, and then carried over by hand in a rubber bucket to the washing house. The after-separating house contains a number of after-separators so that it can hold several days' supply of waste acid.

Recent improvements.

During the first years of the present century a number of important improvements were introduced at the Royal Gunpowder Factory, Waltham Abbey, into the methods of manufacturing nitro-glycerine, as also into the other processes carried out there. Those relating to the manufacture of gun-cotton have been mentioned in Chapters XII and XIII. Major (now Lt.-Col. Sir) F. L. Nathan was the Superintendent, and Mr. J. M. Thomson the Manager, and the nitro-glycerine plant was under the charge of Mr. W. Rintoul. The far-reaching alterations have been dealt with by the first two named of these in the *Journal of the Society of Chemical Industry*, 1908, p. 193.

Washing.

The operation of washing the nitro-glycerine would appear to be a comparatively safe one as the material is neutral or alkaline, and it is only subjected to agitation by means of compressed air; yet there have been a considerable number of fatal accidents in washing houses. H.M. Chief Inspector of Explosives in his Special Report No. 162 on the explosion at Faversham on November 9, 1903, gives a list of nine, which had occurred in Great Britain alone, and

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there was another one at Hayle on January 5, 1904 (Report No. 164), as well as a considerable number in other countries. One possible cause of some of these catastrophes was the presence of the loose air-pipe, which was simply laid on the bottom of the tank; it is quite conceivable that the jarring of this pipe on to the bottom of the tank might in exceptional circumstances cause an explosion. The air-pipe is now carried down the outside of the tank from above the level of the liquid and is burnt on to the under surface of the bottom of the tank. Holes are pierced through at intervals, and there is a hole in the end of each branch of the air-pipe so arranged that any nitro-glycerine, that has lodged in the pipe, will be blown out again into a shallow depression which slopes down to the outlet.

The wooden casing of the washing tanks has also been done away with. It was always possible that a small leak might be formed through which nitro-glycerine would pass and soak into the wood and there set up a dangerous decomposition, and nitro-glycerine was always liable to get spilt or splashed on to the wood.

Abolition of cocks.

Another possible source of danger was the presence of the numerous cocks through which the nitro-glycerine had to pass. Friction might be caused if the cock stuck, or if the nitro-glycerine froze in or around it; also if the hole through the key of the cock were not quite straight, there might be a pocket in which nitro-glycerine could lodge and set up decomposition. Soft rubber tubing has now been substituted for the cocks, arranged as is shown in Fig. 38, which, however, still shows a wooden casing to the tank. The soft rubber tube, *d*, is fixed over the outlet lead pipe, and is kept closed by slipping it over the hollow lead plug, *e*, through which a small current of air is passed whilst the nitro-glycerine is being washed. When the charge is ready to be run off, the air is shut down, and the rubber tube kinked in the hand and pulled off the plug. The flow of the nitro-glycerine can be controlled by pinching the tube with the hand. The skimming tube, *c*, is also of soft rubber; the hard and heavy skimmer has been done away with. This skimming tube has since been improved by widening it at the mouth funnel-wise and providing it with a rubber handle.

It has been suggested that the explosions in washing tanks may have been caused by the generation of electricity by the friction of the air when passing through the jets in the air-pipes. But air or other gas cannot produce electricity by friction, as was shown by Faraday.[1] It is only when the air carries with it particles of solid matter or liquid globules that any charge is formed, and then only if the solid or liquid matter be itself non-conducting. The nitro-glycerine is surrounded on all sides by conductors; on its upper surface by soda solution, and everywhere else by lead, so that any charge would be rapidly discharged, especially as the nitro-glycerine is kept in motion and is

[1] "Experimental Researches in Electricity," Series XVIII., *Phil. Trans.*, January 1843.

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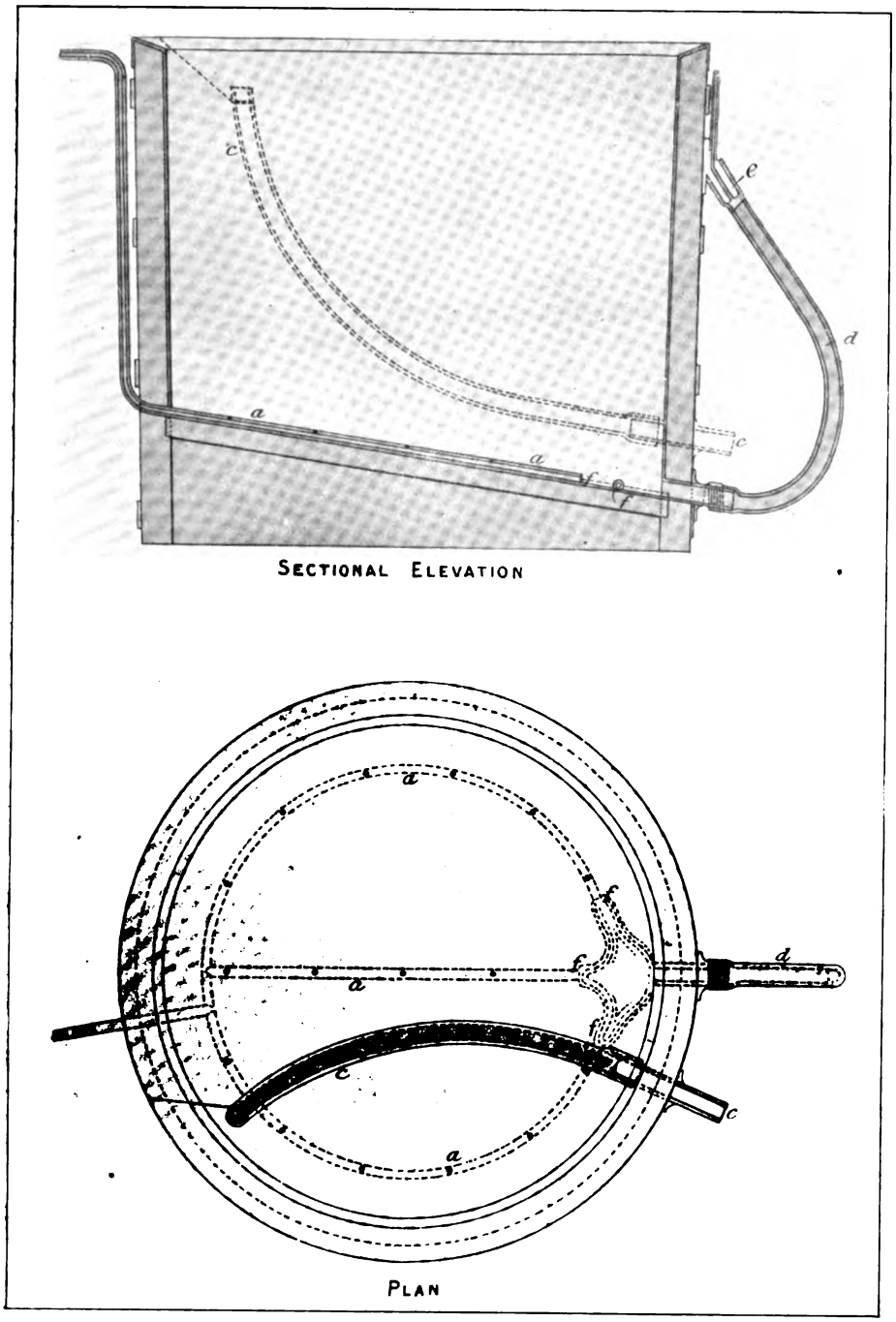

FIG. 38. Nitro-glycerine Washing Tank

a, Air-pipe
c, Skimming tube for wash-waters
d, Outlet pipe for nitro-glycerine
e, Hollow lead plug for end of *d*
ff, Holes in ends of branches of air-pipe

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mixed with drops of the soda solution. Experiments carried out at Ardeer failed to detect any charge of electricity.[1]

Fume hoods. The pre-wash tank is constructed in the same way as the final washing tank; the principal difference lies in the arrangements made for conducting away the fumes. The air rising from the pre-wash tank carries some nitric acid with it as well as fumes of the nitric esters of glycerine; the tank has a fixed lead cover with an opening, which is kept covered with a small rubber flap, and there is a fume pipe through which the fumes are drawn by means of a jet of air or steam. From the washing tank the air carries away only vapour of water and nitro-glycerine, consequently the lead top is unnecessary: it is merely provided with a hood of rubber cloth shaped like a large inverted funnel, the stem of which passes out through the roof and is provided with an air jet to keep a current of air going in an upward direction during the whole of the time of the washing. The removal of the fumes of nitro-glycerine makes the work much less trying to the workmen.

Plugs for air holes. In the pre-wash tank the air-holes in the bottom are bushed with small perforated ebonite plugs to prevent the rapid enlargement of the holes, but in the final washing tanks these small plugs are unnecessary as the wear is very slow.

Softening the washing water. A very hard stony deposit consisting mostly of calcium carbonate used to be formed on the inside surface of the washing tank, due to the action of the soda solution on the hard water employed. This was another possible source of danger. The formation is now prevented by softening the water before use. There is a large tank in the charge house above the level of the nitrating house, and in this sufficient water is treated each day to suffice for all the washing operations of the next day. Enough lime and sodium carbonate is added to precipitate the bicarbonate and sulphate of calcium and the magnesia, and the water is well agitated and allowed to settle over night.

Washing tanks should be made wide and shallow, because a reduction in the depth of the liquid greatly diminishes the time required for the separation of the nitro-glycerine from the water. At the Royal Gunpowder Factory comparative trials were carried out with two different designs of tank, the proportion of water to nitro-glycerine and all other conditions being kept constant. The depth of liquid only was varied by having the tanks of different diameters. The results were:

Total depth of liquid	Mean time of separation
27¼ in.	34½, 28½ secs.
18½ in.	10, 9½ „

Washing operations. In the pre-wash tank the nitro-glycerine is usually washed about four times at a temperature of about 18° C. The first three washings are with water only, but the last with some soda, so as to remove all but a small quantity

[1] *See S.R.*, 156, p. 8.

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of the acid. The nitro-glycerine is then sent down a gutter to the washing house, where the final washing is carried out. The number and duration of the washings vary considerably in different works, but the following scheme is a good one:

1st	washing	15	minutes	with	dilute	soda	($3\frac{1}{2}$ per cent.	Na_2CO_3)
2nd	,,	30	,,	,,	,,	,,	,,	,,
3rd	,,	45	,,	,,	,,	,,	,,	,,
4th	,,	15	,,	with	softened	water	only	
5th	,,	15	,,	,,	,,	,,		

Temperature of washing 30° C., proportion of soda solution or water to nitro-glycerine 4 : 10 by weight.

Labyrinths.

All the wash-waters from the pre-wash and final washing tanks are run through labyrinths before they pass to the wash-water settling tank, and from the latter they again pass through a labyrinth before they reach the pond. The labyrinth consists of a long lead tank open at the top and provided with a number of transverse partitions so arranged that the water has to flow alternately over one and under the next. The bottom is inclined gently to a central channel, which runs the whole length of the vessel; there is also a fall towards the exit end. Most of the globules of nitro-glycerine collect in this central channel, and can be drawn off through a rubber tube arranged in the same way as the delivery tube of the washing tank. Since the introduction of these labyrinths at Waltham Abbey the amount of nitro-glycerine that is recoverable from the wash-water settling tank is only $1\frac{1}{2}$ per cent., whereas formerly it was about $4\frac{1}{2}$ per cent.

Nitrator-separator.

In those parts of the plant where the nitro-glycerine is mixed with strong acid, *i.e.* the nitrator and separator, it is not possible to make use of delivery tubes of rubber, such as have been substituted for cocks in all other parts of the nitro-glycerine plant. Yet cocks are specially dangerous here as the acid nitro-glycerine is more liable to spontaneous decomposition than when it is neutral or slightly alkaline. In January 1901, this danger was brought home at the Royal Gunpowder Factory in a very forcible manner: shortly after the charge had been run out of the nitrating apparatus an explosion occurred in one of the earthenware cocks leading to the drowning tank. If the apparatus had contained the charge, a serious accident must inevitably have occurred. This led to the idea of removing the nitro-glycerine at the top of the nitrator instead of at the bottom; a method, the accomplishment of which was rendered more easy by the fact that the nitro-glycerine separates out at the top of the charge. The simplest way to effect this was to raise the whole of the contents of the apparatus, so that the nitro-glycerine would flow over a suitable arrangement in the cover and run by gravity into the

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pre-wash tank, and the best method for raising the level was to introduce waste acid from a previous charge at the bottom of the vessel.

The form of plant adopted to carry out this principle is shown in Fig. 39, and is protected by English Patent No. 15,983, dated August 8, 1901, taken out in the joint names of Nathan, Thomson, and Rintoul. The separation of the nitro-glycerine from the acids takes place in the same vessel as the nitration, and for this reason the inventors call it a "nitrator-separator." It consists of a cylindrical lead vessel, *a*, with a bottom sloping in one direction, and containing cooling coils and air-pipes, the number of which depends on the size of the vessel. The cooling coils enter and leave through the sides just below the surface of the nitrating acid, as also do the air-pipes, *g*. The cooling water is led in and out again through one main pipe controlled by a single cock, and the coils, *h*, branch away from this main pipe inside the vessel. The supports for the coils are of lead, and are formed by loading up between the turns; this arrangement obviates the use of lead-covered iron supports, and entirely does away with interstices in which nitro-glycerine or sulphate can lodge. The cover is conical, and is burnt on to the cylindrical portion; it terminates in a cylinder, *e*, of small diameter open at the top and provided with glass inspection windows, *f*; the only other fitting in the cover is a gland, through which the thermometer, *s*, passes. A pipe, *k*, opens out of one side of the cylinder, and from this another pipe, *m*, branches for carrying away the fumes, suction being produced by means of an air-jet. At a little distance beyond this fume pipe *k* opens out to a gutter leading down at an incline to the pre-wash tank. The pipe, *d*, for introducing the mixed acid into the apparatus, as well as the waste acid for the displacement, enters the vessel at the bottom. In order to prevent any nitro-glycerine getting into the acid supply pipe it is carried vertically downwards below the bottom of the vessel and rises again into it. There are two branches, *b*, *c*, leading out of this pipe, each with an earthenware cock; *b* leads to the waste-acid egg, and *c* to the drowning tank.

Manipulation of nitrator-separator.

The waste acid from the previous charge having been run out of the vessel, the cock on the nitrating-acid tank is opened, and the acid is allowed to run into the nitrator-separator by opening the cock on the acid supply pipe, *d*. As soon as the acid has all run in, the cock on the nitrating-acid tank is closed as well as that on the acid supply pipe, and the acid having been brought to the desired temperature by means of the cooling coils the injector is inserted through the open top of the apparatus, and the nitration is commenced. The temperature of the cooling water, which flows through the coils is regulated so that the total time of nitration for any given charge is kept constant within fairly narrow limits both winter and summer. To enable this to be done the water is refrigerated when necessary. The advantages of using refrigerated water are that nitration is completed in a reasonable time, loss of nitric acid

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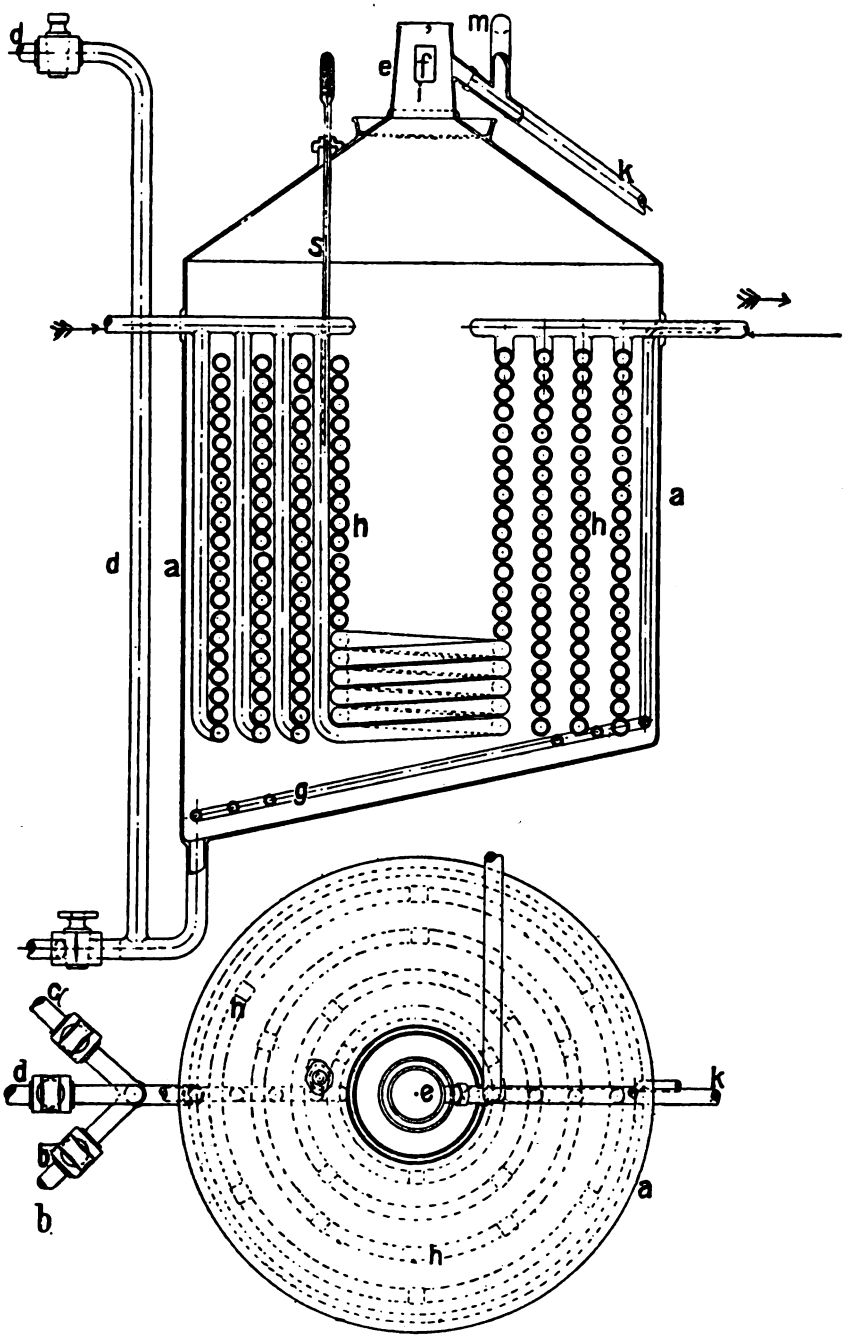

FIG. 39. Nitrator-Separator for the Manufacture of Nitro-glycerine (from *S.S.*)

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due to volatilization is reduced, and the time of nitration being constant the operations of the factory can be carried out in a systematic manner. The volatilized nitric acid is carried away to a Guttmann condensing tower provided with a circulating arrangement for the liquid; the fumes are thus condensed and about 18 lb. of nitric acid of specific gravity 1·32 are recovered per ton of nitro-glycerine produced. When nitration is completed, the injector is removed, and the nitro-glycerine is allowed to separate for a few minutes. The cock leading from the displacement waste-acid tank is then opened, and waste acid is allowed to enter the apparatus at the bottom by opening the acid supply pipe. The rate of inflow of the displacing acid can be regulated with the utmost nicety, so as to allow of the nitro-glycerine flowing over through the gutter to the pre-wash tank as it separates. The dividing line between the clear nitro-glycerine and the acid is watched through the inspection windows.

The nitrator-separator is left full of waste acid until it is required for the nitration of another charge. The result of this is that no part of the interior of the apparatus is exposed to acid fumes, and its life is greatly increased. In the old form of plant, in which this could not be done, and the coils entered through the cover, it was necessary to remove the cover and the coils as often as once in every three months to repair them. The new form of apparatus was in use for two and a quarter years without being opened up, and then the whole of the interior including the coils and air-pipes was found to be as good as new, and no repairs of any kind were required. As a precaution the cooling coils are tested every week by air pressure before commencing work; any leak would be detected at once by the escape of air bubbles through the waste acid.

Cooling coils. It is well to arrange the exit pipe from the coils so that the water in them is under a slight vacuum. If a small leak does develop, the acid will then enter the coils where it will be drowned by the large volume of water, and the defect will be shown by a rise in the temperature of the water leaving the coils. In Germany several explosions have been ascribed to the bursting of the coils, but no such accidents appear to have occurred in England. It has been proposed by the Explosive Works, Dr. R. Nahnsen and Co. of Hamburg, to use chloroform, carbon tetrachloride, or other similar chlorine derivatives for circulating through the coils,[1] but this does not appear to be necessary provided that reasonable precautions are taken.

Prevention of after-separation. The after-separating house has for some time ceased to exist at the Royal Gunpowder Factory. Its abolition was rendered possible by the fact that the addition of water to the waste acid not only prevents the formation of more nitro-glycerine, but also absorbs any that exists as minute globules in the waste acid.[2] Originally only 2 per cent. of water was added to the

[2] Ger. Pat. 31,837, July 6, 1910; *S.S.*, 1912, p. 36.

[1] Nathan, Thomson and Rintoul, Eng. Pat. 3020, February 9, 1903.

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waste acid, as this quantity was found to be sufficient at the normal temperature of storage, 10° to 15° C., to prevent any further separation. But on January 15, 1906, a fatal accident occurred with a drum of nitro-glycerine waste acid, which was part of a consignment sent by the Explosives and Chemical Products Ltd., to Messrs. F. W. Berk and Co. In consequence of

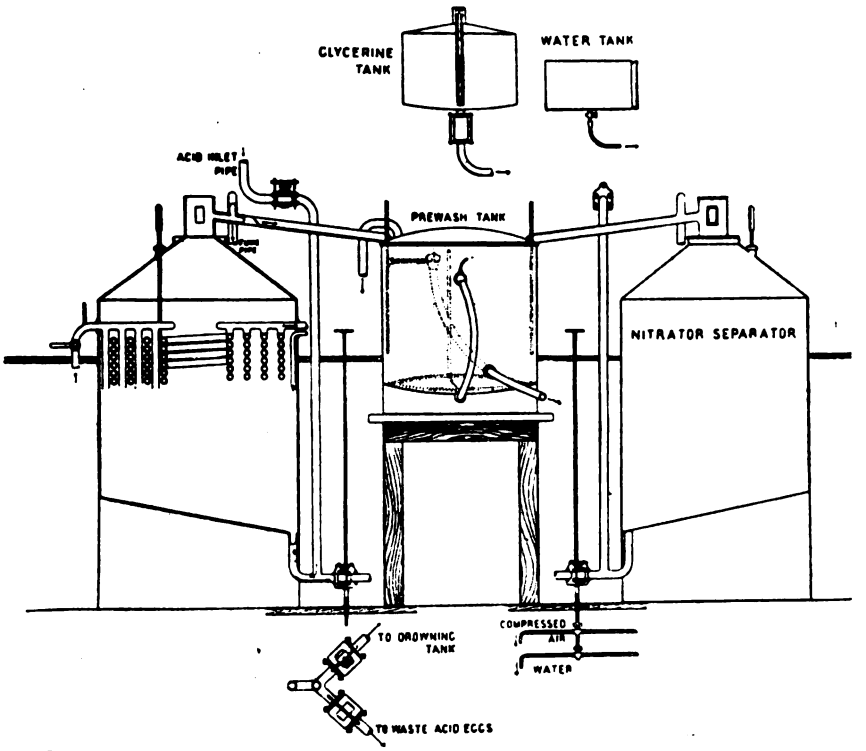

FIG. 40. Waltham Abbey Nitrating-House Plant

this further experiments were carried out at Waltham Abbey, which are given in detail in Special Report No. 174 of H.M. Chief Inspector of Explosives. It was then found that in order to prevent further separation of nitro-glycerine, when the temperature of the waste acid is reduced to 0° C. it is necessary to add 5 per cent. of water. The fact that when the temperature is reduced the solubility of nitro-glycerine in waste acid is considerably diminished should be kept constantly in mind. In Germany, where large variations of temperature are more liable to occur than in England, there have been several accidents due to the further formation of nitro-glycerine on the surface of acid that had been subjected to after-separation for a considerable time.

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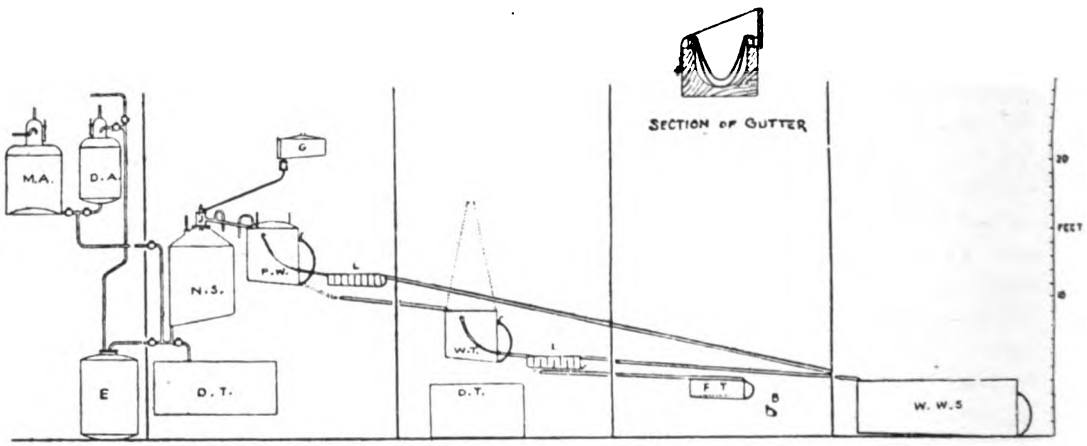
However the waste acids are treated, they should not afterwards be allowed to fall to a very low temperature, and the denitration should take place as soon as possible. If after-separation has taken place without the addition of water, the acid should afterwards be kept at a higher temperature than that at which the after-separation was effected.

The method adopted for dealing with the waste acids in the nitrator-separator is as follows: The waste acid is allowed to remain in the vessel until this is required for another nitration, any nitro-glycerine separating in the interval being displaced in the usual way into the pre-wash tank. Further separation is promoted by cooling down the waste acid. When the nitrator



Charge House | Nitrating House | Washing House | Filtering and Mixing House | Wash Water Settling House

M.A. Mixed Acid Tank
D.A. Displacing Acid Tank
E. Egg

G. Glycerine Tank
N.S. Nitrator Separator
D.T. Drowning Tank
P.W. Pre-wash Tank
L. Labyrinth

W.T. Washing Tank
L. Labyrinth
D.T. Drowning Tank

F.T. Filter Tank
B. Burette

W.W.S. Wash Water Settling Tank

FIG. 41. Diagram of Nitro-glycerine Plant at Waltham Abbey

is to be emptied, every trace of nitro-glycerine is removed from the surface of the acid, and the quantity of waste acid required for the displacement of a subsequent charge is then run out of the nitrator into an egg, and blown into the displacing acid tank in the charge house. To the remainder of the waste acid in the nitrator 2 per cent. of water is then added, the contents of the nitrator being strongly agitated meanwhile by means of air. The waste acid is then sent into an egg and blown up to a tank in the denitrating house. As a further precaution all waste acid is kept at a temperature of about 15° C.

The new Waltham Abbey plant is shown diagrammatically in Figs. 40, 41. One great advantage of the plant is that the elevation of the nitrator above the wash-water settling tank is less than half what it was with the old style of

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plant, viz. 16 feet instead of 33½ feet.[1] The separating and after-separating houses are dispensed with, with the result that the factory occupies less space, and there are fewer pieces of apparatus.

The safety of the manufacture is increased by the absence of cocks, and by the removal of the nitro-glycerine from contact with the acid as soon as it has separated from it. This is an especially great improvement over the procedure in the factories where the separator is in a different house to the nitrator, for there the acid nitro-glycerine has to flow down a long gutter from one house to the other. The presence of cooling coils during the separation is also an advantage. As fewer men are required to work the plant the risk to personnel is correspondingly reduced.

The diminution of danger during separation is a matter of considerable importance as there have been a number of disastrous explosions in nitro-glycerine separators. On February 18, 1904, the separator at the Cliffe Factory started to fume violently and then exploded, causing the death of four men and much structural damage.[2] At Avigliana, in Italy, a similar accident occurred in April 1912, and although the men in the house were able to escape before the explosion, it caused another house to blow up, and two men were thereby killed. In July 1912, a few days after the separating house had been rebuilt, it blew up again. This time the nitro-glycerine caught alight, but again the men in the house were able to escape before the remainder of the charge exploded ; no one was killed, but the material damage amounted to £8000. Similar cases of charges taking fire in the separator have occurred in Mexico. An explosion, due to violent decomposition of nitro-glycerine in a separator, took place on March 1, 1911, at the factory at Umbogintwini in South Africa ; it was ascribed to the use of defective glycerine made locally from whale oil. In 1907 a German nitro-glycerine factory was destroyed by an explosion originating in the separator.

Drowning arrangements.

The drowning cock is controlled by means of a long rod terminating in a handle situated on the operating platform. By turning this handle through a quarter of a circle not only are the contents of the nitrator-separator allowed to run into the drowning tank, but at the same time compressed air is turned on to agitate the contents of the tank, and water is also admitted. The drowning tank is always kept full of water, and is provided with an overflow. This drowning arrangement has the advantage of simplicity, and the continuous supply of cold water keeps down the temperature due to the mixing of a large

[1] It has been proposed to reduce the necessary fall in the nitro-glycerine factory still further by causing the nitro-glycerine to rise from the bottom of the washing tanks through rubber tubes by the weight of a sufficiently high column of water introduced above (Wharton, Shacklady and Curtis's and Harvey, Ltd., Eng. Pat. 23,871, October 14, 1910). Messrs. Curtis's and Harvey have erected a plant with all the vessels for the different operations in the same building, so that the separating, washing, filtering, and measuring of the nitro-glycerine into boxes can be carried out without running it down long gutters to other buildings.

[2] *See S.R.*, No. 167.

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volume of acid with the water, and also allows of a smaller drowning tank being used than would otherwise be necessary.

The regulations of the German Trade Guild (§ 10) are somewhat similar. It is there laid down that the drowning tank must have a capacity equal to at least five times the volume of the acid, and is to be provided with stirring arrangements and a water inlet at the bottom of the tank of such a size that the acid will be rapidly displaced and no heating of the nitro-glycerine will take place. The drowning tanks must always be kept with the proper quantity of water in them. The water inlet and the air for stirring must be turned on simultaneously with the drowning cock, or must be so arranged that they can be operated from a place of safety outside the traverse. In some cases these cocks are so arranged that they are all operated simultaneously by compressed air, which can be turned on from several different points,[1] but it is not advisable to make such arrangements too complex, as they are not only liable to fail, but through some combination of peculiar circumstances they may act wrongly in an emergency, and so whilst preventing an explosion in one house, cause one in another.

Acids and yields.

Before oleum could be obtained at a reasonable cost, it was usual to use an acid made by mixing about 5 parts of C.O.V. with 3 parts of concentrated nitric acid (sp. gr. 1·50). At Waltham Abbey 8 parts of the mixed acid were used to nitrate 1 of glycerine, but in some other works a smaller amount of acid was employed, often 7½ parts to 1 of glycerine.

Theoretically 100 parts of glycerine should give 246·7 parts of nitro-glycerine, but for several reasons this yield is never attained in practical manufacture. The average yield at the Royal Gunpowder Factory over a series of eight years was 214¼ per cent., but after the introduction of the nitrator-separator and other improvements it was 220·2 per cent. as an average of two years' working with the proportions just mentioned. There is practically no oxidation of the glycerine, consequently the reaction may be represented by the following Table :

Before nitrating			After nitrating		
		Per cent.			Per cent.
$C_3H_5(OH)_3$	100		$C_3H_5(NO_3)_3$	246·7	
H_2SO_4	480	60·0	H_2SO_4	480·0	73·5
HNO_3	273	34·1	HNO_3	67·6	10·3
H_2O	47	5·9	H_2O	105·7	16·2
	800	100·0		653·3	100·0

[1] *See* Lesser, *S.S.*, 1907, p. 48.

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The water present in the nitrating acids performs no useful function. It might be eliminated, and acid used as follows :

Before nitrating			After nitrating		
		per cent.			per cent.
$C_3H_5(OH)_3$	100		$C_3H_5(NO_3)_3$	246·7	
H_2SO_4	266·6	52·3	H_2SO_4	266·6	73·5
HNO_3	242·9	47·7	HNO_3	37·5	10·3
H_2O	0	0	H_2O	58·7	16·2
	509·5	100·0		362·8	100·0

But it is more usual to use an acid containing 1 to 2 per cent. water. The following results have, for instance, been recorded by :

	Soddy	Chalon	Hofwimmer
Acid :			
H_2SO_4	58·4	57·3	52·5
HNO_3	40·0	41·3	46·5
H_2O	1·6	1·4	1·0
Proportion Acid : Glycerine . .	6·12, 5·88	6·2	6·3, 5·3
Yield	232, 236	232	228, 221

The results given by Soddy were obtained with a nitrator-separator at a factory in Mexico ; [1] those by Chalon in a similar plant in the dynamite works of Boceda, in Italy.[2] Hofwimmer's figures were obtained from laboratory experiments in which the proportion of acid to glycerine was varied through a wide range ; [3] the maximum yield was obtained with the proportion 6·3 : 1, but the most remunerative proportion at the prices of materials assumed was 5·3 : 1. At Waltham Abbey, with a proportion 6·13 : 1, the yield for a period of nearly two years was 229 per cent.

The differences between the yields generally obtained and the theoretically possible yield of 246·7 per cent. is due to the influence of various factors. The practical yields are generally calculated upon the glycerine as nitrated, whereas this glycerine does not usually contain more than 97 per cent. of glycerol.

The waste acid produced on nitration absorbs a further quantity of the nitro-glycerine, the proportion absorbed depending upon the composition of the waste acid. A still further quantity of the nitro-glycerine

[1] A. & E., March 1911.
[2] *Explosifs modernes*, 1911 p. 222.
[3] C-Z., 1911, 35, p. 1229.

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disappears in solution in the wash waters from the pre-washing and washing operations.

The solubility of nitro-glycerine in acids of varying composition formed the subject of numerous experiments at the Royal Gunpowder Factory.[1] When nitro-glycerine is added to a mixed acid it first dissolves unchanged, but part of it is at once decomposed with the formation of other esters, such as glycerol trisulphate, the production of which may be represented by the reversible reaction: $C_3H_5(ONO_2)_3 + 3H_2SO_4 \rightleftharpoons C_3H_5(SO_4H)_3 + 3HNO_3$. The nitro-glycerine dissolved as such was determined by shaking out rapidly with chloroform, and the nitro-glycerine decomposed was estimated by difference. Fig. 42 shows the amount of nitro-glycerine taken up by acid containing water and nitric acid in the constant ratio 1·1 : 1 and varying percentages of sulphuric acid. It will be seen that portions of the curves are represented by shaded lines. This indicates that on attempting to saturate acids in this zone oxidation of the glycerine radicle occurred, and the results were vitiated. An uncontrollable reaction would set in if special precautions were not taken; no acid of a composition in or near this zone should ever be allowed to come in contact with nitro-glycerine in a manufacturing operation. Fig. 43 shows the results that were obtained with acids in which the ratio of sulphuric acid to water was kept constant at 5·8 and the nitric acid was varied. In Fig. 44 the ratio of sulphuric to nitric acid was kept constant at 10·4, and the water was varied. Fig. 45 was obtained with mixtures of sulphuric acid and water only; here again oxidation took place with acids of 50 to 85 per cent. strength. All these solubility determinations were carried out at 20° C. It will be seen that all the curves with mixed acids show a distinct minimum, which points to the fact that there must be a certain composition of acid which will be the most economical to use.

Time of separation.

The time that the nitro-glycerine takes to separate from the acid is liable to vary within wide limits; when the separation is carried out in a special separator, it may be anything from a quarter of an hour up to several hours. Long separations are very inconvenient as they disorganize the whole of the work of the factory. In the early days of the industry they were generally attributed to impurities in the glycerine, and probably with justice. In the Boutmy system of manufacturing nitro-glycerine the glycerine was dissolved first in sulphuric acid, the solution was cooled and then a mixture of nitric and sulphuric acids was added. But as a result of the action of the concentrated sulphuric acid on the glycerine and the impurities in it, products were formed, which greatly impeded the separation: no nitro-glycerine was taken off until twenty-four hours had elapsed, and then the acids were transferred to carboys or other vessels, where further separation occurred and might continue for a month.[2]

[1] *See* Nathan and Rintoul, *loc. cit.*

[2] For full particulars of this process and its disadvantages, *see S.R.* 48, January 1883.

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Since the introduction of good distilled glycerine, one cause of long separations has been eliminated, and the source of the trouble is to be sought now rather in the acids. A large amount of suspended matter in the acids causes

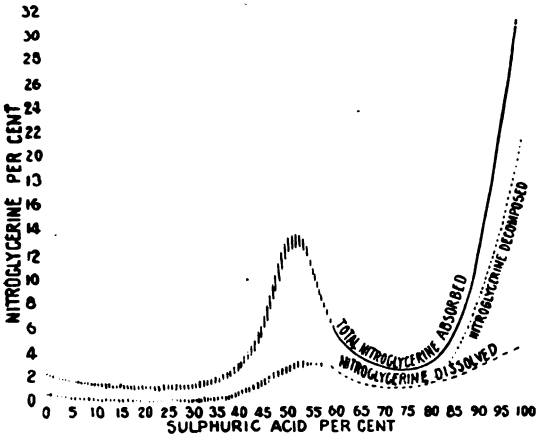

FIG. 42

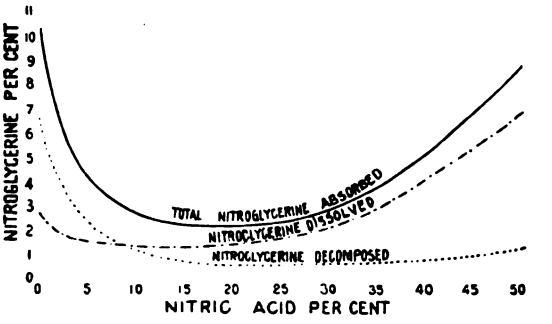

FIG. 43

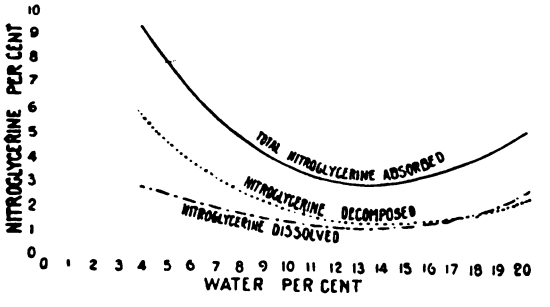

FIG. 44

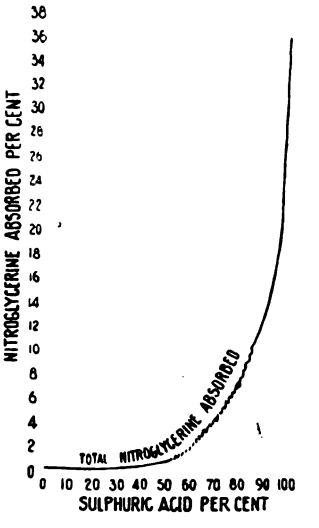

FIG. 45

FIGS. 42–45. Solubilities of Nitro-glycerine in Acids

the formation of numerous small drops of nitro-glycerine, which do not readily coalesce, and consequently take a very long time to separate. Hence the importance of allowing the acids to stand for some days after mixing in order to allow time for the insoluble impurities to settle out. These consist mostly

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of the sulphates of lead, iron and aluminium. But during the nitration process a further quantity is precipitated, mostly lead sulphate, which is considerably less soluble in dilute acids than in concentrated, and this freshly formed precipitate is probably more injurious, as it has not had time to be converted into larger aggregates. The time of separation increases with increase in the percentage of water in the waste acid; this is no doubt due partly to the larger amount of lead sulphate precipitated, but may also be caused partly by the retardation of the nitration reaction by the presence of the water. Just the same trouble with long separations is liable to occur with the nitrator-separator or any other form of plant. It is due to the formation of an emulsion of the one liquid in the other, and is intimately connected with the phenomena of surface tension, but the matter has not been investigated sufficiently to allow of a full and satisfactory explanation. The formation of an emulsion can be prevented by the addition of various substances to the charge; thus R. Moeller, in Ger. Pat. 171,106, claimed the addition of 0·05 to 0·2 per cent. of the weight of glycerine of various fatty substances, such as paraffin, vaseline, the higher fatty acids and their esters. The slow separations have also been ascribed to the presence of silicates, and especially gelatinous silicic acid, and the addition of 0·001 per cent. of sodium fluoride has been proposed to destroy them.[1] The Westfalisch-Anhaltische Sprengstoff A. G., in their Ger. Application 38,595 of December 2, 1911, on the other hand claim the addition of a small quantity of a silicate, such as kaolin or talc, and the Rheinische Dynamitfabrik adds both silica and hydrofluoric acid or sodium silico-fluoride.[2]

Either paraffin or sodium fluoride undoubtedly accelerates the separation, but the use of such substances is attended with various disadvantages. It is not possible to remove the last traces of them from the nitro-glycerine and they may have a deleterious effect on the stability; this applies especially to nitro-glycerine that is to be used for the manufacture of military smokeless powder, which may have to be kept for a long time under adverse conditions. If sodium fluoride is used the hydrofluoric acid given off during the nitration and the denitration of the acids attacks the plant to some extent, but the quantity used is too small to make this trouble a serious one.

Conveyance of nitro-glycerine.

Before the invention of dynamite and blasting gelatine nitro-glycerine was sent long distances in the liquid state. The dangers involved led to numerous accidents, as was inevitable. In America Mowbray froze the material for the purposes of transport, but then it had to be thawed again before use, as it is too insensitive in the frozen state. In Europe liquid nitro-glycerine is now no longer used as such, but in America it is employed for "blowing" oil-wells, for which purpose it has to be sent by road, as the railways will not carry it. In the works the principle is adopted of mixing

[1] Eastern Dynamite Co., Ger. Pat. 181,489; C. L. Reese, Am. Pat. 804,817.

[2] Eng. Pat. 14,586, of June 12, 1912.

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it with a solid substance at as early a stage as possible, so that the quantity of liquid nitro-glycerine is reduced to a minimum, but until it has been fully washed and mixed, it must of course be conveyed from one house to another in the liquid state. This is sometimes done in closed trucks or trolleys (*see* Fig. 46). In Germany the tendency is to revert to trolleys on account of the danger of explosions being communicated from one house to another by gutters

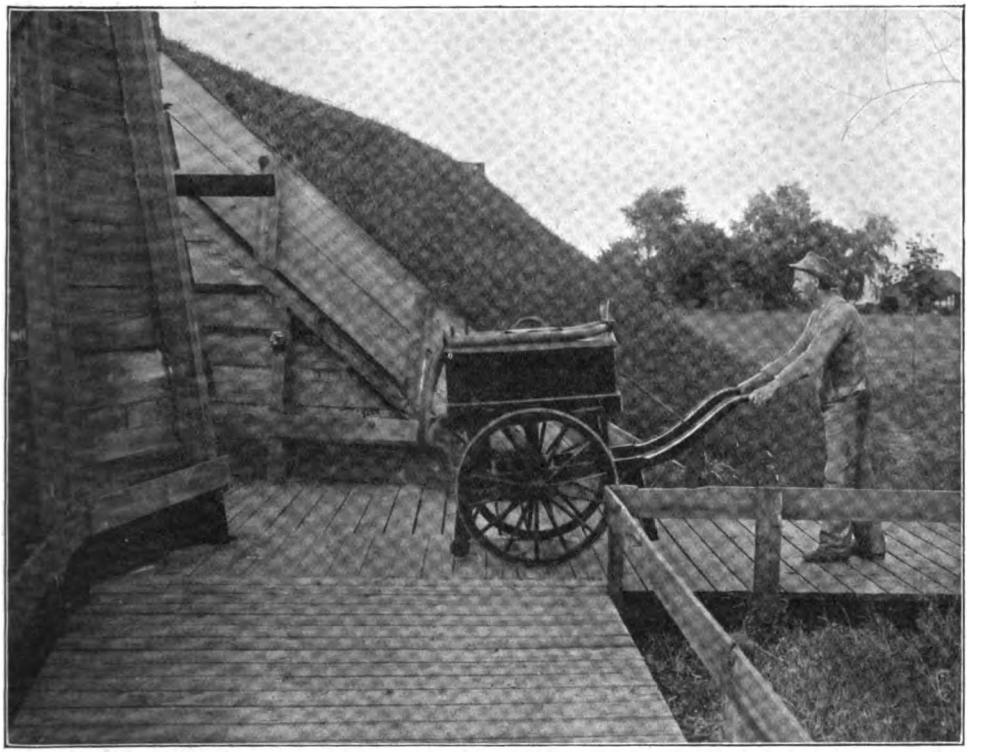

FIG. 46. Truck for Conveyance of Liquid Nitro-glycerine, Repauno, U.S.A.
(By permission of E. I. du Pont de Nemours Co.)

or pipes. Where small quantities only have to be transferred, as from the after-separating and wash-water-settling houses to the washing house, covered buckets of india-rubber, gutta-percha, or papier maché are used, and these are carried in the hand. In England the bulk of the nitro-glycerine is, however, caused to run from one house to another through open gutters, which are usually made of lead. Pipes are not suitable on account of the impossibility of inspecting or cleaning them properly. All wash-waters are also sent down open gutters to the wash-water-settling house, as they carry globules

Gutters

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of nitro-glycerine. The fall of the gutters should not be less than about 1 in 65 ; they should be free from sharp turns and from all inequalities in which nitro-glycerine can lodge. At the Royal Gunpowder Factory they are joined by butt-welding, as this gives a much smoother surface than lap-welding. In order to prevent the nitro-glycerine from freezing in cold weather, the gutter connecting the nitrating house with the washing house is provided with an outer jacket (*see* section in Fig. 41), and warm water is circulated in this when the outside temperature is low. The gutter is protected by means of a canvas covering fixed along one edge and laced down on the other,

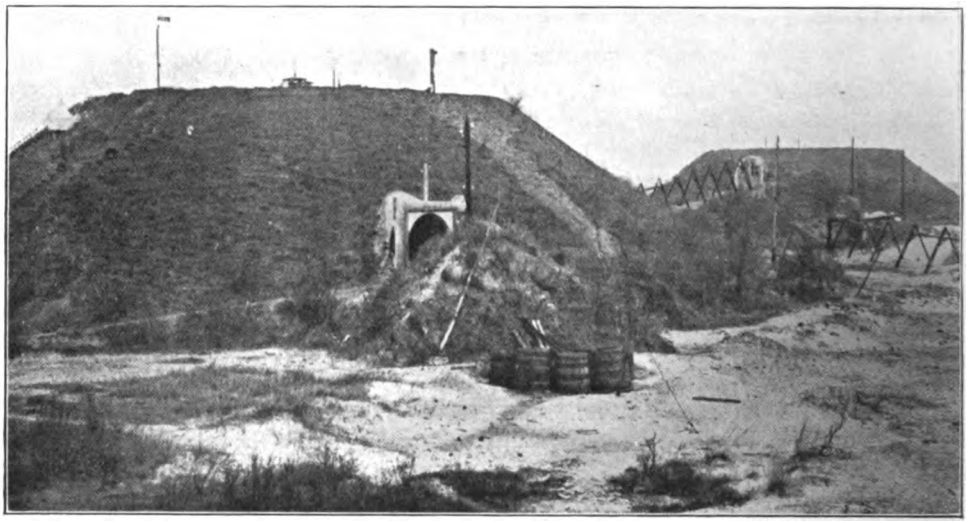

FIG. 47. European Nitro-glycerine "Hills." Forcite Works at Baelen-Wezel
(From *Fabrication des Explosifs*, Brussels, 1909)

so that it can easily be turned back for cleaning purposes. After a charge has been run down, the gutter is wiped along its whole length with a flannel in the direction of the washing house to remove any traces of nitro-glycerine.

When the nitro-glycerine has been mixed with sufficient gun-cotton or other absorbent material to render it non-liquid it is comparatively safe. "Mixed material" for the manufacture of cordite has been transported in very large quantities over considerable distances without mishap. When the nitro-glycerine factory at Waltham Abbey, near London, was destroyed by an explosion on May 7, 1894, supplies were obtained from the Nobel Factory at Ardeer, in Scotland, in this state until a new factory was built. Gun-cotton in the wet state was sent from Waltham Abbey to Ardeer, and was there dried and mixed with the requisite quantity of nitro-glycerine and

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returned by sea, and so the manufacture of cordite at Waltham Abbey was not brought to a standstill. Similarly, when the nitrating house at Curtis's and Harvey's works at Cliffe, in Kent, was blown up on February 18, 1904, gun-cotton was sent from there to Waltham Abbey, and was there converted into mixed material and sent back. Messrs. Curtis's and Harvey were thus enabled to carry out their Government contract for cordite, which was urgently required for the South African War. The Düneberg Factory, near Hamburg, which makes the nitro-glycerine smokeless powder for the

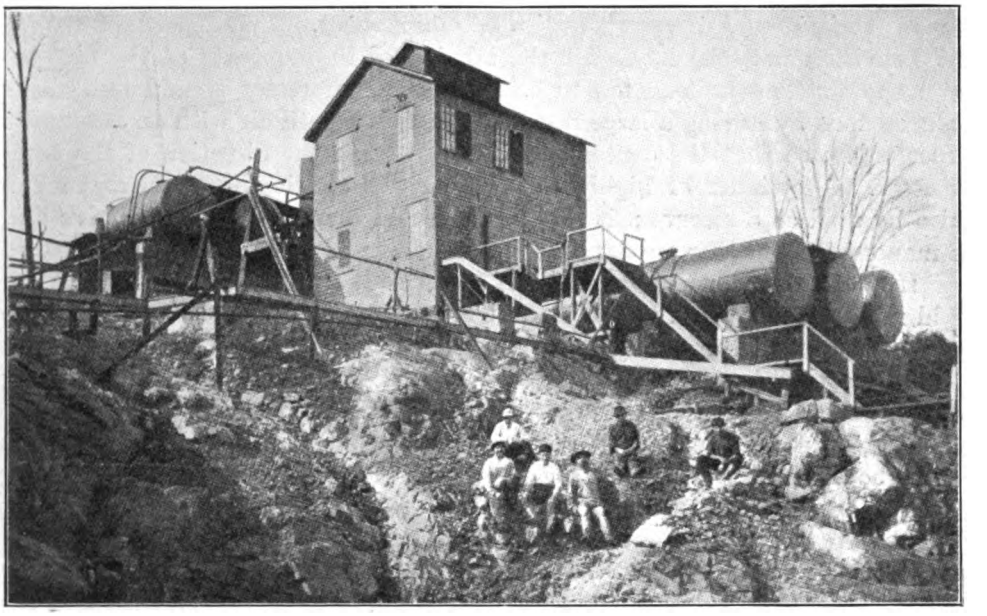

FIG. 48. American Nitro-glycerine Hill, Haskell, U.S.
(From *Appleton's Magazine*)

German Navy, obtains all its mixed material from the neighbouring dynamite works at Krümmel, which was the first nitro-glycerine factory erected by Nobel outside Sweden.

Location of factory.

Nitro-glycerine factories are often built on rising ground in order to provide a fall from each house to the next without having to make the nitrating house of great height. With the nitrator-separator, however, the difference of level between the top of the nitrator and the bottom of the wash-water settling tank need not be more than 16 feet, which can easily be provided for on a flat site. One great disadvantage of placing a nitro-glycerine factory on the top of a hill is that it is very likely to be struck by lightning, and if that occurs it does not seem that any system of lightning conductors, however complete,

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will prevent the explosion of the nitro-glycerine and the consequent total destruction of the building. There have been numerous cases of such catastrophes in Germany and South Africa. In consequence of this the danger buildings of the Hoppecke dynamite factory have been built underground in a hill, and Bichel has put forward similar proposals.[1] This matter is treated in more detail in Chapter XXXIII.

That part of the works in which are situated the buildings for the manufacture of nitro-glycerine and other specially dangerous operations should be separated from the rest by a fence, and no one should be allowed within the "danger area" unless his duties take him there.

Air supply. Provision must be made for the stirring of the contents of the nitrator and the washing tanks, etc., in case the air compressor should fail. This can be done by having a large reservoir for compressed air with an automatic inlet valve, so that the contents cannot escape in the direction of the compressor. A cylinder of highly compressed carbon dioxide or nitrogen can also be used as a reserve; it should be provided with a reducing valve and a manometer, or other appliance, to show how much it contains.

Thunder-storms. If a thunder-storm pass over the factory all work must cease in drying and mixing houses, and the men must retire to the mess-room or other place of safety. In the nitrating house no fresh charge should be started whilst there is a thunder-storm anywhere near. All men must leave the building except one to look after the separation, and one for the nitrator if a charge be in the process of nitration. If the storm becomes very threatening, these also should leave after stopping the operations. Charges in the washing tanks may be left with the air turned on. In Germany it is laid down that the electric light and power wires are to be disconnected.

Limit boards. Every nitro-glycerine house, like all other danger buildings, must have a board in the entrance showing the maximum number of workmen and the greatest quantity of explosives that may be in it at one time. In Germany the following are the greatest numbers of men allowed, exclusive of carriers:

Nitrating house	2
Separating house	1
Washing house	2
After-separating house	2
Wash-water house	2
Denitrating house	2

Use-lists. At the Royal Gunpowder Factory, Waltham Abbey, Use-lists are also posted up, showing the total number of loose articles that are allowed in each house. This is a very valuable institution as there is no doubt that many accidents have been caused by the dropping or falling of some heavy implement, or by the use of some unsuitable tool. It has been found possible to limit the

[1] *S.S.*, 1910, p. 182.

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number of loose articles to those which appear in the Table given below. These only are allowed.

General precautions.

It need scarcely be said that the most scrupulous cleanliness and tidiness must be observed in all nitro-glycerine houses. Any nitro-glycerine that may be spilt should be wiped up immediately with a flannel.

The men in the nitro-glycerine section should have special clothes of a different colour from those of other danger building men. There must be no pockets. The boots must be changed on entering a danger building; those worn inside must have no nails or other parts made of iron. Keys and other implements, that have to be brought near the buildings, are to be made of gun-metal or other soft material.

USE-LISTS AT WALTHAM ABBEY

	Nitrating House	Washing House	Wash-water House	Filtering and Mixing House
Bags, rubber	—	—	—	1
Bottles, gutta-percha	—	—	—	12
Buckets, rubber	3	6	6	—
Covers, bucket, gutta-percha	—	6	6	—
Flannels	4	3	2	2
Gauntlets, rubber	1	—	—	—
Gauntlets, leather	—	—	—	2
Overshoes, rubber	4	3	2	—
Socks	—	—	—	2
Thermometers	3	3	2	—

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CHAPTER XVII

LOW-FREEZING NITRO-GLYCERINE

Freezing of nitro-glycerine explosives : Effect of additions : Super-cooling : Dinitro-glycerine : Dinitro-chlorhydrin : Dinitro-acetin : Dinitro-formin : Tetranitro-diglycerine : Dinitro-glycol : Nitroisobutyl-glycerine nitrate

Freezing of nitro-glycerine explosives.

ONE of the greatest drawbacks attaching to nitro-glycerine explosives is the liability of nitro-glycerine to go solid at moderately low temperatures. The melting-point of pure nitro-glycerine is 13·3° C. or 56° F.,[1] but it can often be kept even in large quantities for considerable periods at temperatures much below this without solidifying, for it shows in a high degree the phenomenon of super-cooling. In the solid state it is much less sensitive to the detonative effect of fulminate, and this is a great source of danger, for frozen cartridges are liable to remain in the bore-hole partly or entirely unexploded, and in the subsequent operations they are very likely to be fired by a blow with disastrous results. Whether frozen nitro-glycerine is more sensitive to blows than when liquid the evidence is somewhat contradictory. H.M. Inspectors of Explosives[2] tried the effect of a falling weight of 5 lb. on little cylinders of dynamite ½-inch diameter and ½-inch high, placed between gun-metal discs, and found that whereas the unfrozen material was sometimes exploded with a fall of 30 inches, the frozen dynamite was never exploded with a single blow of the weight falling 48 inches, but a feeble explosion was produced at the second blow. Later on further experiments were carried out with other nitro-glycerine explosives.[3] Thin slices of the explosive about the size of a shilling and about 0·2 inch thick were placed between brass plates 1 inch square and 1/8-inch thick. The slice thus sandwiched was placed on an anvil, and a 58-lb. weight was allowed to fall on the upper brass plate. The critical or probable exploding points under these conditions were found to be about as follows :

	Unfrozen	Frozen
Blasting gelatine . .	12′ ..	1′
Gelatine dynamite . .	7′ to 8′ ..	6′ to 7′
Dynamite	1′ ..	—

The figures give the number of feet of fall of the weight which caused explosion.

[1] Kast, *S.S.*, 1906, p. 225 ; Nauckhoff, *S.S.*, 1911, p. 124 ; Hibbert, 8th *Int. Cong. App. Chem.*, vol. iv., p. 37. [2] *A.R.*, 1879. [3] *A.R.*, 1889.

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The dynamite was in slices about the size and thickness of a sixpence. It was also found that frozen dynamite was very liable to detonate when it was ignited, whereas the plastic material merely burnt away under the same conditions. Some hard frozen blasting gelatine laid on a sloping board and fired at with a rifle at 20 yards' range detonated powerfully, whereas unfrozen cartridges under similar conditions did not explode, and cartridges of the explosive frozen only slightly were merely scattered.

On the other hand, Will,[1] in falling weight and shooting experiments, found the frozen nitro-glycerine explosives less sensitive in all cases. The differences in the case of the falling weight experiments were probably due to the use of very much smaller quantities of explosive by Will. It is the increased resistance offered by the frozen explosives that makes them more dangerous to manipulate. If a very thin layer be used it is the resistance of the supporting surface that comes into play and not that of the explosive, and when fired with a detonator also, the hardness of the material has but little influence. But miners have to do with whole cartridges of explosive and that these have special dangers is shown by the accidents that occur in spite of the warnings that have been issued repeatedly and the regulations that require the use of proper warming-pans. Thus, in the annual report of H.M. Inspectors of Explosives for 1911, the following cases are cited :

No. 2, Jan. 4. Man injured whilst ramming home a frozen charge of gelignite.

No. 32, Jan. 16. A man inserted an iron spike into a cartridge of Samsonite preparatory to attaching the detonator. The cartridge was probably frozen. Two injured.

No. 35, Jan. 3. Man injured breaking a frozen cartridge of Samsonite in two by hand.

No. 66, Jan. 4. A labourer was about to charge a shot-hole when he fell and knocked the explosive against the rock. Apparently the gelignite had not been thawed sufficiently or had become hard again. Man injured.

No. 92, Mar. 22. A man was in the act of breaking a frozen gelignite cartridge with his hands when it exploded. Two injured.

No. 106, Mar. 10. Whilst a miner was handling a congealed gelignite cartridge it exploded and injured him.

No. 117, Mar. 25. A miner dropped a " hard " gelignite cartridge on a tram-rail and it exploded. One injured.

No. 119, Mar. 25. A charge of undoubtedly hard frozen Samsonite exploded whilst being rammed home with a wooden rammer. Two injured.

No. 158, Apr. 11. A chargeman was making a hole for a detonator in a Rippite cartridge when it exploded. Apparently the cartridge had been rather hard, and he rested it on the ground and was pressing or knocking the pointed end of the steel nippers into it. One injured.

Similar cases have occurred in other years, but not always with the same fortunate absence of fatal injuries. The following Table shows how certain classes of accident are much more frequent at those times of the year when nitro-glycerine is liable to be frozen. Only those accidents in which an explosive containing over 10 per cent. of nitro-glycerine was involved are shown here.

[1] *Zeits. Berg-, Hütten-u. Salinenwesen*, 1905.

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	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sep.	Oct.	Nov.	Dec.
Ramming or stemming charge .	3	3	4	3	1	1	—	—	—	—	1	1
Boring into unexploded charges	1	2	1	—	1	—	2	—	1	—	—	2
Striking unexploded charges in removing debris . .	2	2	1	—	—	—	1	—	—	—	—	1
Total of above causes, 1911 .	6	7	6	3	2	1	3	—	1	—	1	4
Total in past 11 years . .	68	76	83	51	34	23	24	12	20	17	28	53

In addition to these there were up to the end of 1911 107 accidents in thawing cartridges of frozen nitro-glycerine explosives, causing death to 84 persons and injuries to 139 others. It is true that all except one of these accidents would have been avoided, if the explosives had been thawed in the regulation manner. The one exception was due to the thawing of some unstable explosive, the heat test of which had been masked by the addition of mercuric chloride.

Effect of additions.

These special dangers and the trouble in having to keep the explosives in heated magazines during cold weather, or of thawing them and keeping them thawed up to the time of using them, as well as the great difficulty in preventing the workmen thawing them in an irregular manner has caused endeavours to be made to manufacture nitro-glycerine explosives which will not freeze so readily. For this purpose use is made of the fact that when a substance is dissolved in a liquid the freezing-point is depressed in accordance with the equation $\Delta = E \cdot \frac{m}{M}$, in which Δ is the depression of the freezing-point produced by the addition of m grammes of a substance of molecular weight M to 100 grammes of the solvent, and E is a constant, which represents the depression produced by 1 gramme-molecule. It can be calculated by the formula $E = \frac{RT^2}{100W}$ in which R is the gas constant (= 2), T the absolute temperature of the freezing-point and W the latent heat of fusion.

The behaviour of nitro-glycerine when cooled was investigated by Nauckhoff,[1] and was found by him to be quite normal. He determined the latent heat of fusion as 23·1 cal.,[2] and hence E = 70·5. The following Table gives some of the depressions of the freezing-point observed and calculated by Nauckhoff:

[1] *Ang.*, 1905, pp. 11, 35.

[2] H. Hibbert and G. P. Fuller found the latent heat to be 33·2 cal. (*J. Am. Chem. Soc.*, 1913, p. 978).

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Substance Dissolved	Molecular Weight	Grammes per 100 g. N/G	Depression of Freezing-point	
			Observed	Calculated
Nitro-benzene	123	0·637	0·30°	0·37°
,,	,,	1·334	0·73°	0·76°
Dinitro-benzene	168	0·644	0·23°	0·27°
,,	,,	1·508	0·59°	0·63°
Trinitro-benzene	213	1·935	0·56°	0·64°
Dinitro-toluene	182	1·057	0·37°	0·41°
Dinitro-naphthalene	218	0·707	0·23°	0·24°

Nauckhoff also determined the freezing-, or rather melting-points of a number of mixed explosives :

Nitro-glycerine	100	100	100	100
Nitro-benzene	19·7	10	5·9	5·7
Nitro-cellulose	10	8	5·1	7·0
Freezing-point	1·0°	5·0°	7·5°	9·0°

Nitro-glycerine	50	50	50	50	50	50	50	50	50	50	53
Nitro-cellulose	5	5	4	5	5	5	5	5	5	5	5
Ammonium Nitrate	40	35	40	35	40	34	40	40	40	40	42
Nitro-benzene	5	10	—	—	—	—	—	—	—	—	—
Dinitro-benzene	—	—	5	10	—	—	—	—	—	—	—
o-Nitro-toluene	—	—	—	—	5	11	—	—	—	—	—
p-Nitro-toluene	—	—	—	—	—	—	5	—	—	—	—
Nitro-naphthalene	—	—	—	—	—	—	—	5	—	—	—
o-Nitro-phenol	—	—	—	—	—	—	—	—	5	—	—
Aniline	—	—	—	—	—	—	—	—	—	5	—
Freezing-point	5°	2°	6½°	4°	6°	1½°	6°	7½°	6½°	4°	11½°

The freezing-point of the nitro-glycerine used for these experiments was about 10·5°. Taking into account this fact, and that the law of the depression of the freezing-point is strictly true only for dilute solutions, the figures found agree fairly well with those calculated. The low freezing-point of the original nitro-glycerine was due of course to the presence of some impurity in the nitro-glycerine, probably dinitro-glycerine, of which about 8 per cent. would be required to produce this depression. Nauckhoff considers that 10·5° is

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the normal freezing-point of commercial nitro-glycerine, but this no doubt depends upon the composition of the acid used and the proportion of acid to glycerine. There is no doubt that much of the nitro-glycerine manufactured is almost pure trinitrate and freezes near 13°.

The melting-points of nitro-glycerine, dinitro-chlorhydrin and mixtures of them were determined by Kast : [1]

Nitro-glycerine	Dinitro-chlorhydrin	Melting-point	
		Observed	Calculated
g.	g.		
24	0	13·4°	—
21	2·1	9·0°	9·6
21	4·2	6·2°–7·0°	6·1
21	6·3	4·0°	2·6
0	30·8	6·6°–6·8°	—

Kast also gives the " freezing-points," but as the liquids were cooled considerably below the true freezing-points before being inoculated with a crystal, the composition had been altered by the separation of crystalline nitro-glycerine before the temperature rose to a maximum, and this consequently did not correspond with the true freezing-point, which is, of course, identical with the melting-point. Kast observed that nitro-glycerine can also crystallize in another or " labile " form, the melting-point of which is more than 11° below that of the stable form. Freezing-point determinations were also carried out with mixtures inoculated with crystals of this form :

Nitro-glycerine	Dinitro-chlorhydrin	Melting-point	
		Observed	Calculated
24	0	2·7° to 2·9°	—
12	11·5	about −12°	−31·5
18·4	5·4	−7° to − 5°	−8·1
21·6	2·6	−0·8° to − 0·6°	−2·0
0	23·1	5·1° to 5·2°	—

A different sample of dinitro-chlorhydrin was used for this series.

Super-cooling. Nitro-glycerine preparations do not necessarily go solid when the temperature is reduced below the freezing-point, on the contrary they can often be

[1] *S.S.*, 1906, p. 225.

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kept for months at a temperature considerably lower without solidifying. This property of super-cooling is intimately connected with a slow rate of crystallizing, when solidification does start, and this again appears to be related to high viscosity. The rate of crystallization of a given substance depends also upon the temperature; as this is reduced below the freezing-point the rate increases at first, reaches a maximum and then falls again. Nauckhoff gives the following Table: [1]

Substance	Temperature	Super-cooling	Rate of crystallization mm. per min.
Glycerine	0°	10°	0·011
Nitro-glycerine	5°	7·3°	0·145
,,	0°	12·3°	0·183
,,	−4·9°	17·2°	0·267
,,	−17°	29·3°	0·125
Betol	—	—	1 maximum
Guaiacol	—	—	6 ,,
Azo-benzene	—	—	570 ,,
Phosphorus	—	—	60,000 ,,

The rate of crystallization is further reduced, if the nitro-glycerine is gelatinized with collodion, but if it is absorbed in kieselguhr its tendency to crystallize is increased. When a cartridge of a nitro-glycerine explosive has once been frozen, it has a much greater tendency to become hard again as soon as the temperature falls below the freezing-point. This is probably due to the separation of globules of practically pure nitro-glycerine, which only mix again with the impurities and other constituents very slowly.

The first attempts to reduce the freezing-point of nitro-glycerine were with nitro-benzene [2] and nitro-toluene.[3] Unfortunately they not only reduce the sensitiveness of the explosive, a difficulty that can be overcome by the use of a stronger detonator, but also diminish the power and the velocity of detonation. For blasting hard rock these drawbacks are of the greatest importance, but for safety explosives for use in coal-mines, etc., far less so; in fact it is necessary to reduce the power and the velocity of detonation in order to make the explosive safe, and for blasting soft rock too high a rate of detonation is undesirable. Hence various nitro-hydrocarbons are used as constituents of many safety explosives. In order to reduce the freezing-point to any great extent it is necessary that the proportion of dissolved substance to nitro-glycerine should be fairly high, and the greater the molecular weight of the addition, the larger must be its proportion. But substances of

[1] *Ang.*, 1905, p. 16.
[2] Rudberg, Swed. Pat., April 30, 1866.
[3] Volney, Am. Pat., March 5, 1872; Wahlenberg and Sundström, Swed. Pat. 1877.

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very low molecular weight cannot be used because they are volatile. Therefore, in order not to reduce the efficiency of the explosive too much, it is desirable to add some substance that is almost as effective an explosive as nitro-glycerine. There are a number of substances closely allied to trinitro-glycerine, which can be used.

Dinitro-glycerine.

Methods for the manufacture of dinitro-glycerine have been devised by Mikolajczak [1] and the *Zentrallstelle* [2] (*see* p. 542). Will has pointed out that dinitro-glycerine is liable to go solid at quite moderate temperatures, and that it has the further disadvantage that it combines with water of crystallization, is soluble in water and acids and somewhat hygroscopic. To what extent these troublesome qualities disappear when it is mixed with several times its weight of trinitro-glycerine there is no published evidence to show.

Dinitro-chlorhydrin.

Dinitro-chlorhydrin (*see* p. 534) is easier and cheaper to prepare and purify, and is now used to a considerable extent for reducing the freezing-point of explosives. It mixes with trinitro-glycerine in all proportions and gelatinizes collodion cotton equally well. As regards power, Roewer found that there was little difference between explosives made with nitro-glycerine alone and those made with a mixture in which 20 per cent. of the nitro-glycerine had been replaced by dinitro-chlorhydrin. In the following Table the columns marked A are those obtained with the nitro-glycerine explosives, and B those with the mixtures of nitro-glycerine and dinitro-chlorhydrin :

	Guhr dynamite		Blasting gelatine		Gelignite	
	A	B	A	B	A	B
Trauzl Test, c.c.	300	301	555	541	395	384
Ballistic Pendulum, kg.m. . .	74·0	75·9	111·4	111·4	90·8	88·5

The calorimetric figures calculated for 65 per cent. gelatine dynamite (63 per cent. nitro-glycerine or mixture, 2 per cent. collodion cotton, 26 per cent. sodium nitrate, and 9 per cent. cellulose) also give similar results :

	A	B
Heat evolved per kg.	1,244 Cal.	1,278 Cal.
Temperature of Explosion . . .	2,939°	2,835°
Gas produced per kg.	7,168 litres	6,872 litres

Dinitro-chlorhydrin is a constituent of the following explosives authorized for transport by rail in Germany : Gelatin Astralit, Gelatin Wetterastralit, Gelatin Donarit, Gelatin Westfalit, and Perilit.

[1] Am. Pats. 789,436 of September 11, 1906, reissue 12,669 of July 2, 1907, and 830,909 of January 26, 1909.

[2] Ger. Pats. 181,385 and 175,751.

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In order to make a mixture of nitro-glycerine and nitro-chlorhydrin, the chlorhydrin can be mixed with the glycerine, and the mixture nitrated and washed in the usual way.

Dinitro-chlorhydrin is practically insoluble in acids and water, and is not hygroscopic, but has the disadvantage that on explosion it gives off hydrochloric acid, which makes it unsuitable for use underground, unless sufficient of an alkali nitrate or other compound be added to convert all the chlorine into an inorganic chloride. This difficulty does not occur if the third oxygen atom in the glycerine molecule be combined with the radicle of an organic acid instead of chlorine. Vender has found that the acetyl and formyl derivatives, mono-acetin and mono-formin, can be nitrated and give a good yield, provided that the mixed acid contains more nitric than sulphuric acid.[1] Dinitro-acetin, $C_3H_5(NO_3)_2.(C_2H_3O_2)$, he says, can be obtained with a yield of 95 per cent. by nitrating 40 parts of acetin with a mixture of 100 parts nitric acid and 25 of 25 per cent. oleum. Dinitro-formin may be made by heating 100 kg. glycerine with 50 kg. oxalic acid first at 100° and then at 140° to 150°, and then nitrating. The product has a specific gravity of 1·57, contains 15·7 per cent. N and consists of 33 per cent. dinitro-formin and 67 per cent. nitro-glycerine. It is unfreezable and gelatinizes collodion as well as, if not better than, nitro-glycerine.

Dinitro-acetin.

Dinitro-formin.

By treating it in various ways glycerine can be condensed to di-glycerine: $2C_3H_8O_3 = H_2O + (CH_2OH.CHOH.CH_2)_2O$, and this on nitration yields a tetra-nitrate $C_6H_{10}N_4O_{13}$, which reduces the freezing-point of nitro-glycerine just as the other substances that have been mentioned. The formation of di-glycerine was studied in the *Zentralstelle*,[2] and it was found that the conversion was best effected by heat alone. By heating glycerine for seven or eight hours at 290° to 295° some 60 per cent. of di-glycerine is formed together with 4 to 6 per cent. of poly-glycerines. The constituents can be separated by distillation at a pressure of 8 to 10 mm. According to Eng. Pat. 24,608 of October 24, 1910, taken out by Nobel's Explosives Co., W. Rintoul and A. G. Innes, the conversion is best affected by heating at a temperature of 245° to 250° in a current of inactive gas, such as carbon dioxide, which carries away the water formed, and keeps the liquid in a state of agitation.

Tetranitro-di-glycerine.

Claessen, in Eng. Pat. 9572 of 1908, claims the use of a small proportion of alkali; by heating to 275° to 280° with 0·5 per cent. the conversion is effected in a comparatively short time.

Pure di-glycerine boils at 245° to 250° under a pressure of 8 mm.; it is a colourless, sweet liquid readily soluble in water; its specific gravity is 1·33, and it is eleven times more viscous than glycerine. Tetra-nitro-di-glycerine is very similar to nitro-glycerine. A mixture of glycerine with about 25 per

[1] Ger. Pat. 209,943 of April 27, 1906, and *S.S.*, 1907, p. 21.

[2] *See* Will, *S.S.*, 1906, p. 231.

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cent. di-glycerine can be nitrated in the same way as glycerine alone, and the product is unfreezable. Guhr dynamite made with such a nitro-glycerine produced as great an effect in the lead block as ordinary dynamite.

Dinitro-glycol. Dinitro-glycol $CH_2NO_3.CH_2NO_3$ is used by the "Société anonyme d'Explosifs et de Produits chimiques."[1] Its power according to calculation is 4 per cent. greater than that of nitro-glycerine. In the calorimetric bomb the results obtained indicated a superiority of 8 to 20 per cent. according to the method of interpreting the results; by the lead block test the results were about equal. The Société state that at the present high price of glycerine nitro-glycol can be made at a cost not much greater than that of nitro-glycerine. It is more volatile than nitro-glycerine; its specific gravity is 1·496 at 15°.

Nitro-isobutyl-glycerine nitrate. If nitro-methane be mixed with 4 parts of 40 per cent. formaldehyde and a little potassium carbonate or bicarbonate be added, condensation takes place with the formation of nitro-isobutyl-glycerine: $NO_2CH_3 + 3H.COH = NO_2C.(CH_2OH)_3$, a crystalline substance readily soluble in water and alcohol but less soluble in ether. It melts at 158° to 159°.[2] If this be purified by recrystallization and then nitrated with mixed acid, the trinitrate $NO_2C(CH_2NO_3)_3$ is formed,[3] a liquid of specific gravity 1·68 and very low freezing-point. At present it is not of practical importance on account of the high price of nitro-methane, but if an inexpensive method of making this could be devised, it could be used commercially.

[1] *P. et S.*, 16, 1911–12, p. 72.
[2] Henry, *C.R.*, 1899, I., p. 1154.
[3] Hofwimmer, *S.S.*, 1912, p. 43.

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PART VI

SMOKELESS POWDERS

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CHAPTER XVIII

SMOKELESS POWDERS FOR RIFLED FIRE-ARMS

Drying the nitro-cellulose : Alcoholizing : Incorporation : Shaping the powder ; Poudre B : Russian powder : American powder : Spanish powder : Ballistite : Filite : Solenite : German powders : Cordite : Weighing the gun-cotton : Measuring the nitro-glycerine : Mixing : Incorporating : Pressing : Drying : Sporting rifle powders : Axite : Moddite

ALL smokeless powders that have been manufactured up to the present have one important feature in common : every one of them consists largely of nitro-cellulose in some form, and many of them contain only small proportions of other substances. They may be divided into two principal classes : those for use in rifled fire-arms, and those for use in shot-guns. Of the former there are two main divisions : those that contain nitro-glycerine, the nitro-glycerine powders, and those that do not contain it, which are called nitro-cellulose powders, although all the powders contain this substance. Powders for rifled fire-arms are required to burn at a uniform rate and not too fast ; this is achieved by converting the nitro-cellulose into a uniform and dense colloid by mixing it with a solvent. Sporting shot-gun powders, on the other hand, are required to burn very rapidly, and as a rule are only partially gelatinized. For nitro-glycerine powders the solvent generally used is acetone, as it readily dissolves all nitro-cellulose even of the highest degrees of nitration, but if the powder contain no nitro-glycerine the colloid yielded by acetone is too hard and brittle. Consequently for nitro-cellulose powders ether-alcohol is generally used, and the nitro-cellulose must be of such a description that it can be gelatinized by this solvent.

Drying the nitro-cellulose.

The nitro-cotton or other form of nitro-cellulose comes in the wet state from the factory where it is made. For safety some 30 per cent. or more of water is left in it until it is necessary to dry it for further use. The nitro-cellulose may either be in loose form as it is taken from the centrifugal, in which the greater part of the water has been extracted, or it may be moulded into blocks, slabs or cylinders by compressing it in a hydraulic press with a moderate pressure. The advantage of moulding it is that less dust is formed in the drying stoves and during the operation of weighing the nitro-cellulose. The drying is effected by blowing air by means of a fan through a steam heater and then into the stove. The temperature of the air entering the

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stove should not exceed 60° C., nor the temperature inside the stove 40°. The best arrangement of the inlet pipes is to provide them with a number of orifices near the top of the building and to direct the air on to the ceiling. The outlets should be near the floor and should have a larger area than the inlets. The reason for blowing the hot air in at the top of the stove is that when the air takes up water vapour from the nitro-cellulose it becomes heavier and tends to sink; although the water vapour itself is lighter than the air, the cooling produced by the conversion of the water into vapour is so great that the air after taking up the water is considerably denser. Consequently if the air is blown in at the bottom, as is often the case, the fresh dry air tends to rise at once to the top and escape through the outlets before it has done as much drying as it should. The stove should not be unnecessarily tall; inside it should be lined throughout with zinc sheet with soldered joints or other suitable material, in order that there shall be no cracks in which dust may accumulate, and so that the stove can be washed out thoroughly from time to time. If the nitro-cellulose has been moulded into blocks, these should be stood on racks with air spaces between the blocks to facilitate drying. If the material is in the form of loose fibres, it should be laid on trays, preferably of copper wire. In either case the racks or trays should be so arranged that they are connected electrically to earth, as dry nitro-cellulose is very liable to become electrified and a spark may set the powdery material alight. The stoves should not be very near other buildings, as there is always a risk of one catching fire. The stoves are generally constructed of light material. If the nitro-cellulose be in loose fibrous form, it may be dried in twenty-four hours, but if it be moulded, it will take several days. The greatest care must be exercised not to subject the dry nitro-cellulose to friction or blows, especially if it be still warm. The whole stove should be allowed to cool down thoroughly before it is unloaded.

In most instances, when an accident has occurred in a gun-cotton stove, the explosive has merely burnt away extremely fiercely, but without exploding; but on March 10 and 28, 1913, severe explosions took place in stoves situated respectively at Ardeer, in Scotland, and Pitsea, in Essex.[1] In both cases the stoves were being unloaded, and the presumption is that some of the gun-cotton must have been subjected to blows or friction by the workmen. In the former case it is supposed that the explosion was brought about by upsetting one of the racks on which the gun-cotton primers were placed. The explosion caused three other similar stoves in the neighbourhood to explode also, with the result that altogether seven men were killed and ten injured. The explosion of these other stoves was probably caused by the buildings being shaken and wrecked, and perhaps by the racks being thrown down in them also. From this accident the deduction may be drawn that these and

[1] *S. R.*, Nos. 206, 207.

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all other buildings for sensitive explosives should be so strongly constructed that the explosion of a neighbouring building will not wreck them. The racks should be fixed rigidly to the floor.

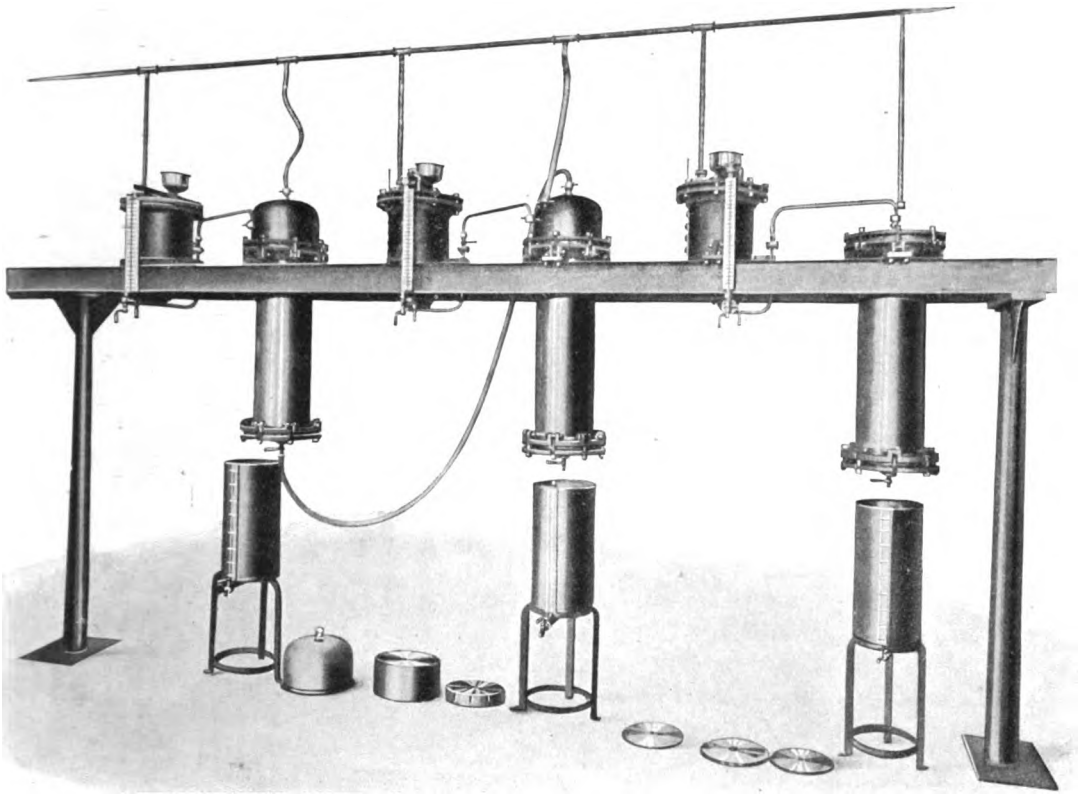

FIG. 49. Alcohol Displacement Plant (Maschinenbau A.-G. Golzern-Grimma)

Alcoholizing.

In the case of powders that are gelatinized with ether-alcohol the troublesome and dangerous operation of drying the nitro-cellulose can be dispensed with, as the water can be displaced by means of alcohol. The wet gun-cotton is packed into a cylinder (*see* Fig. 49), and then alcohol is forced through it by means of compressed air. First, water flows away and is run to waste, then weak alcohol, which is re-rectified, so that it can be used again, and, finally, fairly strong alcohol, which is used again for the preliminary displacement of another cylinder of nitro-cellulose. The alcohol is always introduced at the top of the cylinder as it is lighter than the water; first alcohol from the final displacement in another cylinder, and then strong alcohol. The

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displacement takes three to six hours. When the water has been displaced, the surplus alcohol is removed from the nitro-cellulose by means of a hydraulic press. A type of press much used for this purpose in Germany is shown in Fig. 50. It has two cylinders, which swing round together on one of the columns, so that whilst the contents of one are being pressed, the other can be emptied and filled again. Washing with alcohol has the further advantage that it removes some of the unstable impurities.

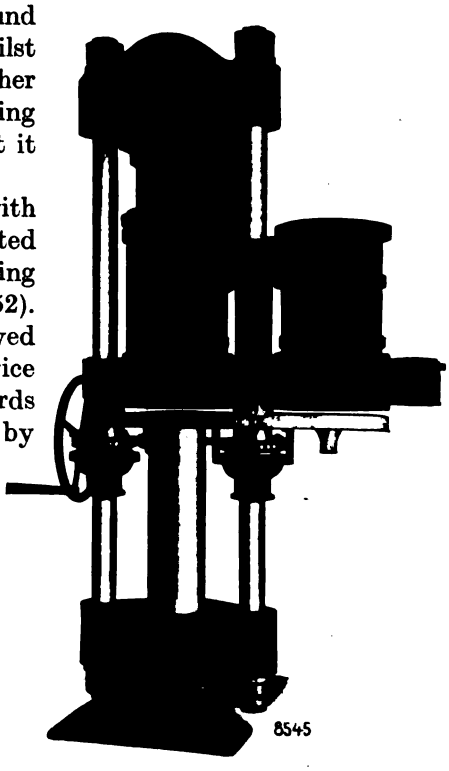

FIG. 50. Press for Alcoholized Nitro-cellulose

Incorporation. The nitro-cellulose is incorporated with the solvent in a machine which is constructed on the same principles as the kneading machines used in bakeries (*see* Figs. 51, 52). It consists of a trough, in which two curved blades rotate in opposite directions, one twice as fast as the other, both going downwards in the centre of the trough and upwards by the walls. First, some of the solvent is poured in to moisten the axles and blades, then the nitro-cellulose and other materials, and finally more solvent. The incorporator is then started and kept running for some hours until the constituents of the powder are thoroughly mixed, the trough meantime being kept covered to prevent loss of solvent. The trough is then tilted up and the blades are made to rotate in the opposite direction. The dough falls into a box or other receptacle, and is taken to the buildings where it is pressed into cords, tubes or strip, or is rolled into sheet, according to the form that it is required to give to the finished powder.

Shaping the powder. The dough is next formed into the desired shape. Formerly it was in many cases rolled into sheets by passing it repeatedly through rolls resembling a paper-maker's calender. The sheets were cut into strips, which were again cut transversely so as to form cubes or flakes. Now it is more usual to press the dough through a die in a press, which is an adaptation of the machine used for making macaroni. It is thus obtained in the form of cords, strips, or tubes ; if desired these can then be cut into flakes of any required thickness.

Poudre B. Poudre B, which was invented by Vieille and adopted by the French Government in 1884 for use in the Lebel rifle, was the first smokeless powder to achieve success in a rifled fire-arm. It is named after the first letter in

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the name of General Boulanger, who was Minister of War at the time. According to an analysis made by Lieut. Wisser, U.S.N.,[1] its composition was :

Insoluble nitro-cellulose	68·2 per cent.
Soluble „	29·8 „
Paraffin	2·0 „

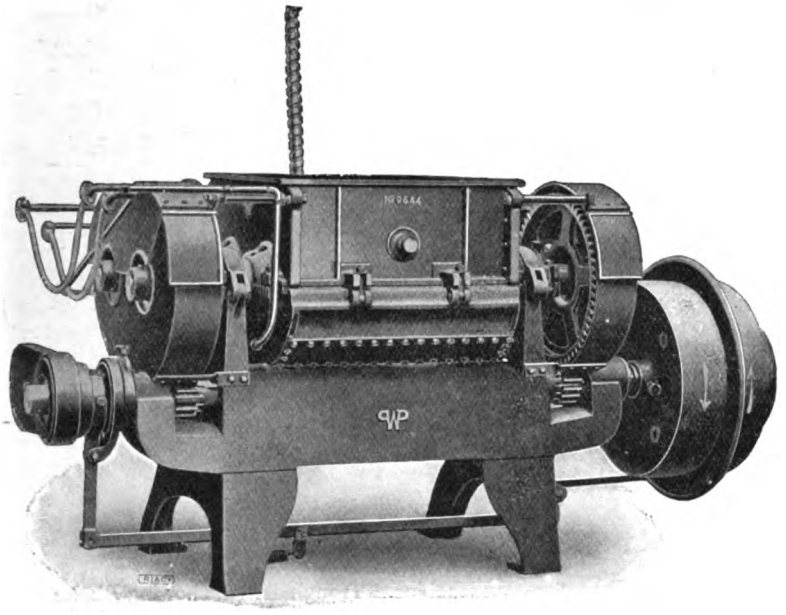

FIG. 51. Incorporating Machine in Working Position
(Werner, Pfleiderer and Perkins Ltd.)

Apparently it was gelatinized by means of acetic ether. The composition was modified several times ; the powder known as Poudre BN consisted of :

Insoluble nitro-cellulose	29·1 per cent.	..	38·7 per cent.
Soluble „	41·3 „	..	33·2 „
Barium nitrate	19·0 „	..	18·7 „
Potassium nitrate	8·0 „	..	4·5 „
Soda	2·0 „	..	3·6 „
Volatile matter	—	..	1·3 „

N stands for Nouvelle. Instead of soda, tannin was sometimes used. The powder was gelatinized with ether-alcohol ; the first analysis was given by Neumann,[2] the second by Weaver.[3]

All other solid constituents were subsequently abolished, and the powder

[1] Worden, *Nitro-cellulose Industry*, p. 962.
[2] *S. S.*, 1910, p. 451.
[3] *Military Explosives*, p. 135.

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consisted only of a mixture of soluble and insoluble nitro-cottons gelatinized with ether-alcohol. In order to improve the stability an addition of amyl-alcohol was introduced in 1896–1897, first 2 per cent. and afterwards 8 per

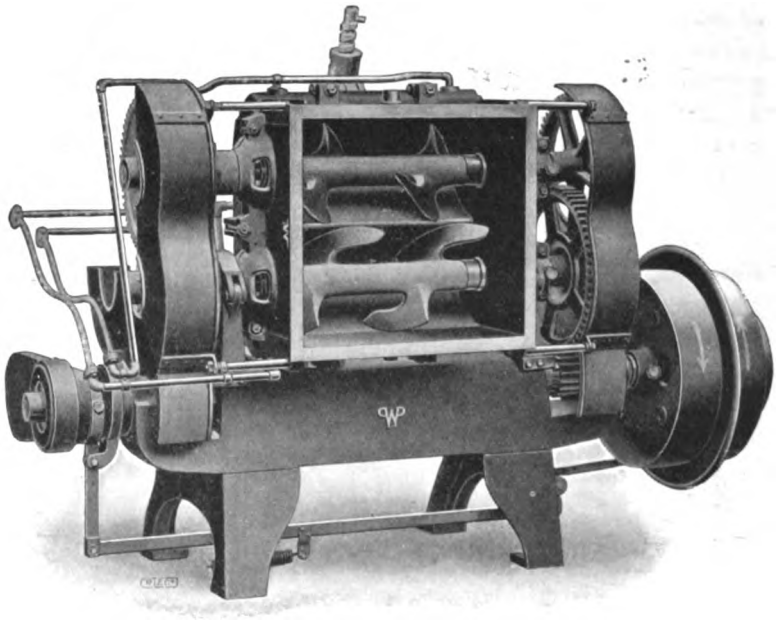

FIG. 52. Incorporating Machine. Trough Tilted, showing Blades

cent. These powders received the names B(AM_2) and B(AM_8) respectively. Now diphenylamine is added.

The nitration of the cotton is carried out partly by the Abel process, which was adopted from Waltham Abbey, and partly in nitrating centrifugals.[1] The cotton used in 1907 was of French production and contained a large proportion of oil. Two sorts of nitro-cotton are made: one with 10 to 15 per cent. soluble in ether-alcohol, and the other with 95 to 99 per cent. After immersion in cold water and wringing in a centrifugal, it is washed five times, five minutes each, with hot water (90° to 95° C.), then it receives ten boils of two hours each, and then further washings of four hours each until the tests are satisfactory. At the Angoulême factory the water is taken from the River Charente. It is very dirty; in 1907 it was not filtered or purified in any way. At Moulin-Blanc the water is much purer, but it is very soft, so ammonium carbonate is added to neutralize the acid. This is likely to have a bad effect on the stability of the nitro-cotton. The two nitro-cottons

[1] *See P. et S.*, vol. xvi., p. 105.

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are mixed in various proportions and sent to the powder works, where the mixture is dried and incorporated with solvent. The dough-like mass is pressed through dies, which form it into ribbons, the size of which depends on the sort of gun the powder is to be fired in. To remove the excess of solvent, the strips are first exposed for some time to the air, then they are dried at 50° for four or five days, and then washed with water, hot or cold, until the proportion of volatile matter has been sufficiently reduced. This washing may have an injurious effect by degelatinizing the surface of the powder.

The powders are given a letter according to the purpose for which they are intended: thus F indicates a small-arm powder from the word "fusil," C one for field-guns from "campagne," SP for siege guns from "siège et place," and GC for coast defence guns from "gros calibre." The powders for naval guns are marked M for "marine," and receive also a figure 0 to 11, according to the gun they are intended for. Thus $BM_0(AM_8)$ is a powder with 8 per cent. amyl-alcohol for the naval 65 mm. gun model 81. The higher indices correspond to the larger guns.

The presence of numerous fibres of ungelatinized gun-cotton in the powder is a bad feature. They make it slightly porous, and consequently facilitate the oxidation of the nitro-cellulose, and this action is further assisted by the partial degelatinization of the surface. The porosity must also affect injuriously the regularity of the ballistics. The solvent tends to escape gradually, and when the percentage has fallen low the material becomes very brittle: it is then liable to break up when ignited in the gun and give very high pressures. On this account amyl-alcohol is now added, which being less volatile tends to escape less rapidly. The extent to which Poudre B is porous is indicated by the specific gravity, which is only 1·52, whereas that of nitro-cotton is about 1·67. Even allowing for the presence of 8 per cent. of amyl-alcohol and 2 per cent. of ethyl-alcohol the density is only reduced to 1·585, and the finished powder contains considerably less solvent than that, for 8 per cent. is the amount of amyl-alcohol added for the incorporation, and much of it is eliminated in the subsequent treatment. In order to restore the ballistic properties of deteriorated Poudre B it used to be subjected to a process called "radoubage," which consisted of reincorporating it with a fresh quantity of solvent, including amyl-alcohol, repressing and re-drying it. It was claimed that this also restored the chemical stability of the powder. To some extent this was probably true, inasmuch as the porosity was reduced to the normal amount, and so oxidation was restrained, but the products of decomposition, which accelerate the deterioration, were left in the powder. Since the *Jéna* disaster radoubage has been stopped, but it was replaced by a process called "remalaxage," which seems to be much the same thing under another name, except that some fresh nitro-cellulose is added.

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Poudre B has earned an unpleasant notoriety by the large number of accidents that it has caused, especially the total destruction of two of France's best battleships with the loss of hundreds of lives, the *Jéna*, in March 1907. and the *Liberté*, in September 1911. These catastrophes were the more striking in that they occurred in Toulon harbour in sight and hearing of the whole city. In the report on the *Jéna* catastrophe accounts are given of twenty-four other spontaneous ignitions of Poudre B, of which five occurred on board ship. There have also been numerous cases of premature explosions and back-flashes during practice, causing large numbers of fatalities, but it is not clear to what extent the powder itself was responsible for these latter accidents.

Russian powder.

The question of smokeless powders was referred by the Russian Government to the great chemist Mendeléeff, who started work upon the problem in 1891 together with a band of able assistants in the scientific laboratory of the navy, which was founded specially for this purpose. Mendeléeff found that it was possible to make a nitro-cotton totally soluble in ether-alcohol, which had as high a percentage of nitrogen as the mixture of soluble and insoluble nitro-cottons used by the French (*see* p. 228). This, which he called pyro-collodion, when gelatinized with ether-alcohol gives a much more uniform colloid than a powder like Poudre B, as may be seen in the micro-photographs reproduced in Fig. 53.

American powder.

The Americans, after experimenting with various sorts,[1] have adopted a pyro-collodion powder for all kinds of guns.[2] In the United States the powder is made up into the form of short cylinders which are pierced longitudinally with small perforations, usually seven. The plant and methods of manufacture are described by Worden (pp. 902–926). The soluble nitro-cotton with 12·6 to 12·8 per cent. N is made as described on p. 159, and boiled to render it stable.[3] The greater part of the water is wrung out in a centrifugal, and the remainder is displaced by alcohol in a hydraulic press. Pressure up to 3500 lb. to the square inch is then applied so as to produce a block weighing about 38 lb., of which 10 lb. is alcohol of 88 per cent. strength. These blocks are

[1] The Maxim-Schüpphaus powders that were used in the American services had the following compositions:

	Per cent.	Per cent.
Gun-cotton	80	80
Soluble nitro-cellulose	19·5	10
Nitro-glycerine	—	9
Urea	0·5	1

They were gelatinized by means of acetone.

The powder for the naval small-arms consisted of nitro-cellulose and the nitrates of barium and potassium, that for the military small-arms contained also nitro-glycerine and a deterrent. (Weaver, *Military Explosives*, 1906, p. 134.)

[2] *See* Schüpphaus, *J. S. C. I.*, 1895, p. 556; Hudson Maxim, *ibid.*, 1897, p. 495; Aspinwall, *ibid.*, 1900, p. 315.

[3] *See above*, p. 169.

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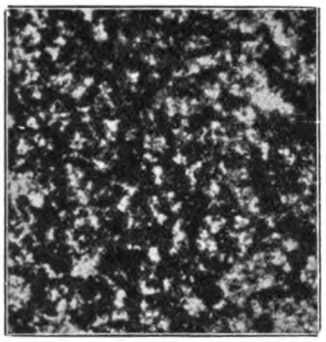
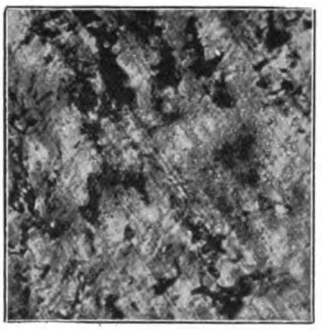
broken up with wooden mallets, and three of them are loaded into an incorporating machine, which is run for about fifteen minutes before any ether is added in order that the lumps may be broken up to a fine powder. Then



Pyroxyline Powder.
Mixture of Soluble and Insoluble Nitro-cellulose



Pyrocollodion Powder

FIG. 53. Microphotographs of Smokeless Powders (Saposhnikoff, *S.S.*, 1907, p. 163)
Sections 0·05 mm. thick. Magnification 150

48·4 lb. of ether are added and 6 oz. of diphenylamine to act as a stabilizer, so that the charge consists altogether of :

Nitro-cotton	84 lb.
Alcohol	26·4 lb.
Water	3·6 „
Ether	48·4 „
Diphenylamine	6 oz.

The incorporator is kept covered to prevent loss of solvent, and incorporation is continued for forty-five minutes. The white, finely comminuted material is then converted into a compact mass by subjecting it to a pressure of 3500 lb. to the square inch in a hydraulic press. By means of another press it is filtered through a 30-mesh iron wire sieve to remove gross impurities. Then it is compacted again in a third press, and by means of a fourth it is squirted through a die, which forms it into a long multi-perforated cord. The dough is so stiff that a considerable amount of heat is generated in passing through the die, but by means of a water jacket the temperature is kept down to 30° or 35°. It is not advisable to reduce the temperature below 30°, because at lower temperatures the cord becomes too hard to be cut into short lengths in the next operation. In order to prevent fall of temperature and evaporation of ether from the warm colloid, the cord is passed at once to the powder cutter, whence the grains drop into a closed receptacle. This is removed to a drying house, where the drying is carried out slowly at first in order not to distort

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the grains too much or make them crack. The finished powder is subjected to special physical tests to ascertain that it is not brittle: the ends of the grains are cut off even and perpendicular to the axis, and then it is subjected to a slow pressure: the length must diminish 45 per cent. before the grain begins to crack.[1] If kept for long there must, however, be a gradual though slow loss of solvent, which will make the grain harder and more brittle. If

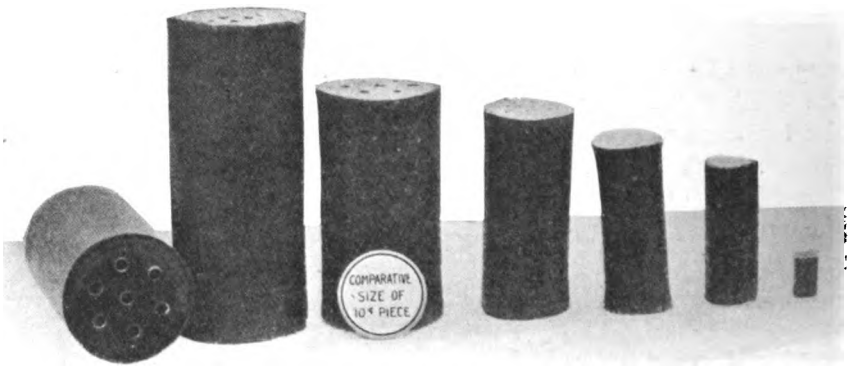

FIG. 54. American Pyrocollodion Powders (from *Appleton's Magazine*)

the powder grains break up in the gun, high pressures are generated, and the gun may be injured or even burst. It is stated that there have been numerous cases of such accidents in the United States, but this has been officially denied.[2] Very large quantities have, however, been re-worked with fresh solvent and an addition of diphenylamine; thus at the powder works at Indian Head in 1910, 829,000 lb. of new powder were made, and 832,000 lb. were re-worked at a cost 35 per cent. of that of the new powder. Altogether nearly 8,000,000 lb. had been re-worked up to the end of 1910.[3] The quantity of solvent in the ordnance powders when new varies from 3 per cent. in that for the 1 pr., up to 6·8 per cent. in that for the 30 cm. 40-calibre gun. The specific gravity of the powder is 1·563,[4] and the cost of production 2*s.* 4*d.* per lb.

The French, Russian, and American Navies are the only ones that use nitro-cellulose powders for their large calibre guns. The other Powers are of the opinion that for this purpose powders containing nitro-glycerine offer decided advantages, but for the comparatively small field-guns and for small-arms every Power except Great Britain and Italy uses nitro-cellulose powder. Nitro-cellulose powders are mostly made of soluble nitro-cotton, because ether-alcohol gives a less brittle colloid than acetone. The powders differ somewhat

[1] Schuhmacher, *S. S.*, 1907, p. 82.
[2] *S. S.*, 1911, p. 136.
[3] *S. S.*, 1911, p. 197.
[4] Schuhmacher, *S. S.*, 1907, p. 82.

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as regards the degree of nitration, also as to the form of the grains, some being rolled into sheets and then cut into small square flakes, others being pressed into cords or tubes and cut off into short lengths; some are coated with graphite and some are not.

Spanish powder.

The Spaniards, after trying a nitro-cellulose powder made at the Rottweil works in Germany, containing about 1 per cent. of camphor and a small proportion of a urea derivative, now make their own powder, which also is of the nitro-cellulose type. For small-arms it is made in the form of flakes, for artillery in long tubes, but they have also experimented with powder in strip form.[1]

FIG. 55. American Rifle Powder (Thörner, *S.S.*, 1907, p. 425)

Ballistite.

In 1887, a few years after the invention of Poudre B, Alfred Nobel invented a smokeless powder in which the fibrous structure of the nitro-cotton was destroyed not by the use of a volatile solvent, but by dissolving it in another explosive, nitro-glycerine. This substance, to which he gave the name ballistite, is indeed blasting gelatine with the proportion of nitro-cellulose largely increased.[2] At first benzene was added to facilitate the solution, and was afterwards evaporated off. A better method of incorporation was discovered by Lundholm and Sayers[3], who place the soluble nitro-cotton and nitro-glycerine in hot water and stir it by means of compressed air. Under these conditions the nitro-cotton gradually dissolves in the nitro-glycerine, or perhaps it would be more correct to say that the nitro-glycerine dissolves in the nitro-cotton. The dough thus produced is then passed between rolls heated to 50° or 60° C., whereby the water is pressed out, and the explosive is made into a sheet. This is folded over and passed through the rolls again, and the operation is repeated until the material has been converted into a uniform colloid. It is then cut into square flakes, generally coated with graphite, and finally it is blended. Various additions have been made at different times to make the powder more stable or to improve its physical properties. The first English patent mentioned camphor, but this was dropped on account of its volatility: diphenylamine, aniline and calcium carbonate have also been used much for this purpose. The powder generally contains 40 to 50 per cent. of collodion cotton and 50 to 60 per cent. of nitro-glycerine.

[1] *See S. S.*, 1908, pp. 154, 248, 283; 1910, pp. 161, 188, 416; from *Memorial de Artilleria*, Feb. and Apr. 1908; Jul., Sept., Oct., Nov., 1909.

[2] Fr. Pats. 185,179 of 1887, and 199,091 of 1889, and Eng. Pat. 1471 of 1888.

[3] Eng. Pat. 10,376 of 1889.

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It has the advantage that the plant required for its production is comparatively simple, but it causes very severe erosion in the guns.

Filite. Ballistite was adopted by the Italian Government soon after its invention, but instead of using it in flake form it was drawn out into cords, and hence was given the name "Filite." Italian ballistite generally consists of equal parts of nitro-glycerine and collodion cotton, together with 0·5 to 1 per cent. aniline; for micro-photos *see* Paterno and Traetta-Mosca, *S.S.*, 1910, p. 145.

Solenite. In consequence of the severe erosion that ballistite causes in the gun, the Italians have also adopted another powder called Solenite. This consists of 33 per cent. nitro-glycerine, 1 to 3 per cent. of a light-coloured mineral jelly, and the rest nitro-cellulose, of which about 50 per cent. is soluble in ether-alcohol and contains 12·4 to 12·6 per cent. N. The powder is gelatinized with acetone and converted into tubular form by pressing through a die, and the tubes are cut into short lengths. The grains are translucent and of a light brown colour, and look somewhat like glass beads.

German powders. The Germans adopted ballistite for their navy in 1898 under the name W.P.C/89: it had the same composition as the Italian Filite, but was made up in the form of square flakes or cubes. W.P. stands for Würfelpulver, *i.e.* cube powder. In 1897 and 1900 other powders were introduced less erosive to the guns. These are blackish-grey in colour, and in composition they appear to be much the same as Solenite or Cordite M.D., except that a little diphenylamine is added as a stabilizer as well as mineral jelly. The powders are made in tubular form and are called R.P.C/97 and R.P.C/00. R.P. stands for Röhrenpulver, *i.e.* tube powder.

The following particulars as to German military powders are given by Berlin: [1]

Nitro-cellulose powders. Colour greyish yellow or brown, resembling glue.

S.P. Flake powder for rifle 98 and carbine 98.

Pl.P.P. (Platzpatronen-pulver). Blank powder for same weapons.

Gesch.Bl.P. (Geschütz-Blättchenpulver). Flake powder for the 9 cm. guns 73, 73/88, and the heavy 12 cm. gun.

Gesch.Bl.P. 03, Gesch.Bl.P. (umg.) } Powders made by re-working Gesch.Bl.P. and Gr.Bl.P. to make them milder and more stable.

Gr.Bl.P. 03 (Grobes Blättchenpulver). Large flake powder for use in the 15 cm. ring cannon and 21 cm. do.

Gr.Bl.P. (umg.). Made by re-working the above.

R.G. 96, R.P. 05 } Tubular powders for use in the field gun 96 n/a (127 mm. long).

R.P. 97 and 99 (Röhrenpulver). For use in the various 10 cm. guns (380 mm. long).

R.P. 07. For the 13 cm. gun.

Man.R.P. (Manöver-Ringpulver). Blank ring powder for field guns.

[1] *Handbuch der Waffenlehre.*

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Nitro-glycerine powders. Colour black due to coating of graphite.

W.P. ($\frac{1}{2}$) (Würfelpulver). Cubic powder, edge of cubes $\frac{1}{2}$ mm. for the 3·7 revolver-cannon.

W.P. ($2 \times 2 \times \frac{3}{4}$). For the 5 cm. gun.

W.P. ($4 \times 4 \times 1$). For the light field howitzer.

W.P. (2). For the heavy field howitzer and 21 cm. bronze mortar.

W.P. ($10 \times 10 \times 1\frac{1}{2}$). For the heavy field howitzer 02, the 15 cm. howitzer, and the 21 cm. bronze mortar.

W.P. ($12 \times 12 \times 12$). For the 21 cm. mortar.

Rg.P. (Ringpulver). Short tubular powder for mortars.

Man.St.P. (Manöver-Sternpulver). A porous powder easily ignited, made in the form of stars, colour grey with yellow spots, for blank cartridges for manœuvres.

Cordite.

About the time of the discovery of Poudre B the English Government appointed a committee to investigate and report upon the subject of a suitable smokeless powder for the British service. Samples were obtained of ballistite and all other available powders, but the committee was not satisfied with any of them, and finally devised a new one, to which the name Cordite was given from the fact that it was made in the form of cords. The composition differed from that of ballistite in that gun-cotton was used, insoluble in ether-alcohol, and this was incorporated with nitro-glycerine by means of acetone which was afterwards evaporated off. Mineral jelly, a semi-solid petroleum product, was added with the idea of lubricating the barrel. It does not have this effect, as it is, of course, entirely consumed in the explosion, but it was a most fortunate addition, as it exercises two most important functions in the powder. Firstly it diminishes the temperature of the explosion and so reduces the amount of erosion of the barrel. At the same time it increases the volume of gas given off and so does not reduce the power of the powder to any great extent. Secondly, it absorbs the nitrous gases which are gradually given off when the powder is stored, and so prevents them from increasing the rate at which the powder decomposes; in this way the mineral jelly adds greatly to the chemical stability of the powder. It also prevents the access of the air to the gun-cotton and nitro-glycerine, and so reduces the amount of deterioration due to oxidation.

The experimental work in connexion with the invention of cordite was mainly carried out in Sir F. Abel's laboratory in Woolwich Arsenal, much of the most important work being done by Dr. W. Kellner, who afterwards succeeded Abel as War Department Chemist. Patents No. 5614 of April 2, 1889, and No. 11,664 of July 22, 1889, were taken out on behalf of the Government by Sir F. Abel and Professor (now Sir) J. Dewar, who were members of the committee, and the same year the manufacture of cordite was commenced at the Royal Gunpowder Factory, Waltham Abbey.

Cordite must be considered one of the most successful smokeless powders, for after a quarter of a century, during which it has been subjected to far more drastic treatment in all parts of the British Empire than the powder

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of any other Power, it is still giving satisfaction. The Germans meantime have adopted and abandoned a number of different powders, and for their naval guns have finally decided upon a powder of the same type as cordite. The two worst defects of cordite are that it erodes the guns badly, especially those of large calibre, and that when stored at a high temperature its life is a limited one. The erosion is not so severe as that caused by the use of ballistite, because the mineral jelly reduces the temperature of the gases considerably. Nevertheless, the wear of the guns was so bad in the South African War that afterwards the composition was modified in order to reduce the temperature further. The proportion of gun-cotton in the powder was increased, and the explosive thus altered was given the name Cordite M.D. (*i.e.* modified).

	Mk. I.	M.D.
Gun-cotton	37	65
Nitro-glycerine	58	30
Mineral jelly	5	5

As regards the chemical stability it is not possible to say whether there is any other powder which would be more satisfactory, as no other one has been subjected to adverse climatic conditions in such immense quantities. It is, however, certain that all foreign Powers find it necessary to exercise constant vigilance over their smokeless powder, especially if it has to be stored at a high temperature; if the vigilance be relaxed, catastrophes inevitably follow sooner or later.

A large proportion of the cordite for the British services is made in the Royal Gunpowder Factory at Waltham Abbey, and it was there that the methods of manufacture were worked out. Under the superintendence of Colonel Sir F. L. Nathan, R.A., a great many improvements were effected in every part of the manufacture, whereby the safety of the workmen was increased, the stability of the explosives was improved, and the cost of production was reduced. Many of these methods have now been adopted by the private contractors, who also supply cordite to the Government.

Weighing the gun-cotton.

When the stove, in which the gun-cotton has been dried, is quite cool, the men go and unload it. The gun-cotton is weighed out in the porch of the stove. These operations require to be carried out with the greatest care, as dry gun-cotton is very sensitive. The men wear nothing on their feet but socks; formerly the gun-cotton was weighed out into brass-lined wooden boxes, but now waterproof india-rubber bags are used. Several explosions have been ascribed to the jar or friction of the edges and corners of such heavy boxes one against the other, especially when the boxes have contained nitro-glycerine. Such accidents can be guarded against to some extent by covering the edges with rubber or leather, but it is better to avoid this danger by using rubber bags; but if nitro-glycerine is to be poured into them it is essential

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that they should be absolutely water-tight, and they should be inspected frequently to ensure this. The scales are of such a design as to reduce friction between the knife-edges to a minimum ; the weights are either attached to the scale so as to form an integral part of it, or they are made of gutta-percha bottles filled with the requisite quantity of lead shot. The quantity weighed out into each bag is that which is required for a charge of the incorporator, or if this be of great size, an integral fraction of it. The necks of the bags are tied up, and they are transported by boat or trolley to the mixing house.

Measuring the nitro-glycerine.

Formerly the nitro-glycerine was weighed out into india-rubber buckets and then poured on to the gun-cotton in the brass-lined boxes. Now, however, it is measured out in a special burette made of lead, which holds the exact quantity required, and is fixed to the floor. It is a small cylindrical vessel with a conical top ending in a narrow neck ; the bottom slopes down to one side where there is an orifice to which a rubber tube is attached, the other end of which can be passed over a lead plug near the top of the burette, when it is not being emptied. Round the outside of the neck is a channel to catch nitro-glycerine that overflows, and this is conducted by a pipe into a rubber bucket, so that it can be returned to the filter-tank. The burette is filled by means of the rubber pipe attached to the filter-tank, until it is quite full, and then the burette is emptied by means of the similar rubber tube attached to it into one of the rubber bags containing dry gun-cotton.

Mixing.

The next operation is to mix the gun-cotton and nitro-glycerine roughly together, and reduce the large primers of the former to the form of powder. At one time this was done by rubbing the material through a $\frac{1}{2}$-inch copper wire sieve, but now a special lead table is made for the purpose. This is pear-shaped and slightly dished out. At one end are a number of $\frac{1}{2}$-inch holes, and underneath is a sort of neck on to which a bag can be attached. The contents of a bag of gun-cotton and nitro-glycerine are placed on the other and larger part of the table ; then a man wearing leather gloves transfers a little at a time to the end where the holes are and rubs it through into the bag below. No unnecessary violence must be used.

Incorporating.

The " cordite paste " thus obtained is next taken to the incorporating house. The interior of the incorporator (*see* Figs. 51, 52) is thoroughly moistened with acetone, the charge of paste is added and the rest of the acetone, and the machine is run for three and a half hours, then the mineral jelly is added and the kneading is continued for another three and a half hours. The quantity of acetone used is about 56 per cent. of the weight of the gun-cotton.

Pressing.

The cordite dough thus obtained is next pressed through a die, which forms it into a cord. The type of press used depends upon the size of cordite that is to be made. The smaller sizes, such as $3\frac{3}{4}$ which is used for rifles, are pressed in a small press with only a single orifice, and the cord as it emerges is wound on to a small drum, which is then taken to the cordite stove for

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drying. The larger sizes are made in large presses which have several orifices, and the large cords as they emerge are cut by hand to the lengths required, according to the size of the cartridges to be made ; these sticks are then laid upon trays, which are conveyed to the stove. Inside the press cylinder above the die is placed a piece of fine wire gauze, through which the dough is made to pass in order to remove from it all foreign material as far as possible. The dough is rammed into the press cylinder by means of a wooden rammer. There is only one pressing operation, whereas the American multiperforated nitrocellulose powder undergoes four.

For pressing cordite in the ordinary round form the die has, of course, a simple round hole. For making tubular cordite a pin is inserted in the centre of the hole. In the case of tubular cordite of small size it is found that the tubes have a tendency to collapse in consequence of the difficulty the air has to pass through a great length of narrow tube. To overcome this difficulty Lloyd and Curtis's and Harvey Ltd. use a perforated pin communicating through the side of the die with the open air.[1]

Occasionally the cordite ignites as it emerges from the press. As a rule no serious damage is done, but on September 17, 1909, an ignition took place at Waltham Abbey whilst pressing cordite Mk.I size 20, which wrecked the press and damaged the building. Two men were injured by broken glass from the windows, which were shattered. The fire was accompanied by two explosions probably of acetone vapour as well as some cordite. The first apparently destroyed the die seating and released the die ; the burning then continued, and the second explosion occurred in the cylinder.[2]

Drying. The cordite stove consists merely of a building provided with suitable racks and heated by means of steam pipes to a moderate temperature, which depends upon the sort of cordite that is to be dried. Cordite Mk.I size $3\frac{3}{4}$ gives off its moisture so readily that artificial heat is not necessary in the summer time. All that is required is to keep the reels in the stove at a temperature of about 15° C. for a few days. The larger sizes are dried at temperatures from 38° to 43° C. for periods ranging up to a fortnight. Cordite M.D. gives off its moisture much less readily than Mk.I and consequently requires to be kept in the stove several times as long ; in the case of the largest sizes the stoving occupies months, and is one of the greatest difficulties that have to be contended with in the manufacture. The moisture in the cordite Mk.I must not exceed 0·4 to 0·6 per cent. according to size, but the percentage allowed in M.D. is considerably more. The size of cordite is given by a figure, which is the approximate diameter in hundredths of an inch of the die through which the cordite has been pressed. Thus cordite size 50 has been pressed through a die about $\frac{1}{2}$-inch in diameter. The thickness of the cord is, however, somewhat less than this, as it shrinks considerably in drying. Various par-

[1] Eng. Pat. 27,700 of November 28, 1910.

[2] *See* A. R., 1909, p. 33.

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ticulars about the various sizes of cordite will be found in the *Treatise on Service Explosives*, Appendices V and VI.

It is usual now to recover as much as possible of the acetone that is given off during the drying. The cordite should therefore be placed in an air-tight receptacle as soon as possible after pressing, and this should be taken to the stove without unnecessary loss of time.

Sporting rifle powders.

The smokeless powders used for sporting rifles are practically the same as those used for military small-arms. Ballistite of a suitable size is employed to a considerable extent, as the erosion is not so very severe in these weapons. Cordite is very largely used: most of the principal explosives manufacturers in England make cordite for the Government, and consequently have all the plant and experience required. Several slight modifications of cordite are also made.

Axite.

Thus Kynoch Ltd. in axite have replaced a portion of the gun-cotton by means of potassium nitrate or oxalates of potassium and barium. A sample that I examined some years ago had the following composition:

Nitro-glycerine	29·7 per cent.
Gun-cotton	63·1 „
Mineral jelly and oil	5·1 „
Volatile matter	0·2 „
Potassium nitrate	1·9 „
	100·0 „

It was made in the form of flat strips. The patents, Nos. 12,892 of June 22, 1905, 15,564, 15,565 and 15,566 of July 26, 1905, cover the use of olive-oil in addition to vaseline or mineral jelly, of flakes and strips with various forms of ribs and knobs to facilitate ignition, and the addition of carbonates. Axite is also sometimes made of a composition resembling that of cordite Mk.I with part of the gun-cotton replaced by potassium nitrate. It is claimed that axite erodes the rifle less than cordite, as the temperature of explosion is lower, and that it does not cause the barrel to rust so much, because the residue remaining in the bore is alkaline.

Moddite

Eley Bros. also manufacture a variety of cordite which they call Moddite. A sample, which I examined, had the composition:

Nitro-glycerine	38·7 per cent.
Nitro-cellulose	56·8 „
Mineral jelly	4·3 „
Volatile matter	0·2 „

Of the nitro-cellulose 34·5 per cent. was soluble in ether-alcohol. It was made in the form of strip.

Nitro-cellulose powders are also used in sporting rifles. They are generally made of soluble nitro-cellulose containing 12 to 12·5 per cent. N gelatinized with ether-alcohol. Sometimes a few per cent. of some other constituent, such as resin, is added. Usually the powders are made in the form of flakes.

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CHAPTER XIX

REQUIREMENTS OF A SMOKELESS POWDER

Rate of burning : Form of powder : Progressive powder : Erosion : Nitro-glycerine *v.* nitro-cellulose powders : Backflash : Muzzle flame

It is required of a powder for rifles or ordnance that it shall give a high-muzzle velocity with moderate pressures, that it shall not cause too much erosion of the bore, and that the ballistics shall be regular, *i.e.* different rounds fired with similar ammunition must give practically the same velocity to the projectile. The speed acquired by the bullet or shell is due to the pressure of the powder gases on its base, as it travels down the bore of the fire-arm, and it is important that the powder shall burn in such a manner that the pressure is suitable during the whole of the time until the projectile leaves the muzzle.

Rate of burning.

Two of the most important facts in connexion with the study of internal ballistics are : (*a*) That the grains of completely gelatinized powders burn away uniformly from the surface, so that they retain their original shape, but get thinner until entirely consumed ; and (*b*) that the rate of burning varies directly with the pressure. From the results of experiments in closed vessels Vieille deduced that the rate of burning v could be calculated from an equation of the form $v = cp^x$, where p is the pressure and c and x are constants. For ballistite $x = 0{\cdot}60$, and for a pure nitro-cellulose powder $0{\cdot}67$. Mansell [1] and Petavel [2] prefer an equation of the form $v = a_0 + ap$, where a_0 is the rate of burning when there is no pressure, and a is the rate of increase of burning per unit of pressure. For cordite $a_0 = 0{\cdot}5$ cm. per sec. and $a = 0{\cdot}018$ cm. per sec. per atmosphere.

That the burning proceeds uniformly by layers is shown by the fact that if a gelatinized powder be fired from a gun, which is too short to allow of the total consumption of the explosive, the remains of the grains thrown from the muzzle are found to be in every way similar to the original grains, except that the dimensions are reduced.

Form of powder.

The result of this is that with a powder made in the form of cords or cubes there is a diminution of the burning surface as the combustion of the charge

[1] *Phil. Trans.*, 1907, 207A, p. 243.
[2] *Proc. R.S.*, 79A, p. 277 ; *S. S.*, 1908, p. 166.

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proceeds, and consequently the pressure falls off rapidly as the projectile approaches the muzzle, although not so much as was the case with black powder, which being porous did not burn entirely by parallel surfaces. In order to overcome this objection other forms are often adopted for the grains of powder. If a strip or flake be used, the width of which is great compared with the thickness, the area of surface remains practically constant until the material is entirely consumed. It has been found, however, that powders made up in these flat forms are liable to give irregular ballistics, and this has been ascribed to the obstacles in the way of regular ignition, when two grains lie flat against one another. Messrs. Kynoch have proposed to remedy this defect by providing the strips or flakes with ribs or knobs.

Constancy of the area of surface can also be attained by making the powder in the form of tubes. There is then no difficulty about the ignition, but the pressure inside the tube is always somewhat greater than outside, because the gases cannot escape very readily, and this excess of pressure may become sufficiently great to split the tubes. If this occur, the ballistics become unreliable, partly on account of the sudden relief of pressure, and partly because the surface is increased in an erratic manner. If the gravimetric density of the powder in the chamber be high, the general pressure is increased and the difference between the pressure inside and outside the tubes is diminished.

If instead of only one perforation there be several as is the case with the American multiperforated powder, the pressure increases as the burning proceeds, and consequently the pressure is maintained at a higher level whilst the projectile is travelling through the forward portion of the bore. This should not be carried too far, because it is not practicable to have great thickness of metal near the muzzle. To prevent the grains splitting in consequence of the great pressure inside them they are cut into short lengths.

The thickness or diameter of a powder should be such that it is entirely consumed shortly before the projectile reaches the muzzle.

Surface treatment.

The relative rate of burning of the powder charge at different instants can also be regulated by submitting the explosive to an operation, wherein the surface layer of the material is modified. Such "progressive" powder is made at Rottweil by treating the grains of nitro-cellulose powder with an alcoholic solution of "Centralite" (dimethyl-phenyl-urea); this causes the outer layers of the grains to burn more slowly, and so causes the chamber pressure to be less, and that further down the bore to be higher. The same method is being tried in France.[1] Another method is to treat the powder in a drum with a solution of 0·1 to 1 per cent. of paraffin-wax dissolved in benzole.

There has been considerable controversy as to the relative advantages and disadvantages of nitro-cellulose and nitro-glycerine powders. The

[1] *See* Florentin, *S. S.*, 1913, p. 32.

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Nitro-glycerine v. nitro-cellulose powders.

advantages claimed for nitro-glycerine powders are that they give more regular ballistics, do not give back-flash when fired, are more powerful, are cheaper to manufacture, and have at least as good chemical stability as nitro-cellulose powders. Their great disadvantage is that the temperature of explosion is high, and consequently the erosion of the bore of the gun is very severe.

In spite of the fact that they erode the guns more, most of the Powers use nitro-glycerine powders in their large guns, and the principal reason for this is that they give more regular ballistics. It is impossible to drive the whole of the solvent out of a colloided nitro-cellulose powder, even though the drying be greatly prolonged, and indeed it is advisable to leave several per cent. in the powder, because otherwise it is too brittle. But this residual solvent is a source of uncertainty, because it gradually diffuses from the centre of the grains or strips, etc., and evaporates, even though the powder be stored in closed receptacles. The loss of this combustible matter makes the powder more powerful, but what is more serious is that the material becomes harder and more brittle, and it may break up when fired, and consequently give high pressures and irregular velocities. The French have endeavoured to overcome this difficulty by adding amyl-alcohol to their Poudre B, but this only diminishes the evil, it does not overcome it, for amyl-alcohol, although considerably less volatile than ethyl-alcohol, still evaporates fairly rapidly.

The addition of a considerable proportion of nitro-glycerine to a powder makes it give up its volatile matter much more readily. Apparently the residual solvent passes from the particles of gun-cotton to the adjacent ones of nitro-glycerine, and diffuses through the latter to the outside of the stick or flake much more rapidly than it can through the colloidal nitro-cellulose. The result is that the percentage of volatile matter can be reduced without difficulty to 1 per cent. or a little more, and if a fraction of this afterwards escapes, it does not alter the composition of the powder materially, and even the loss of the whole of it does not affect the physical properties of the material. The presence of the nitro-glycerine causes it to remain always a tough or slightly plastic mass according to the percentage.

The smaller bulk of nitro-glycerine powders is of some advantage on board ship, where magazine room is limited. The lighter weight of the cartridges also makes them rather more easy to handle. As regards the relative stability of nitro-glycerine and nitro-cellulose powders *see* Chapter XXXIV.

Erosion.

The question of erosion was investigated by Vieille,[1] who showed that the temperature produced in the explosion was the principal factor. He fired charges of various explosives in vessels, which were closed except for a small orifice drilled through a metal plug, which was weighed before and after the experiment. He found that the erosion increased with increase of

[1] *P. et S.*, vol. xi., 1902, p. 157.

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length of the orifice, with decrease of the diameter, and with increase of the volume of gas and the pressure. The influence of the nature of the explosive is shown by the following Table :

Explosive	Pressure kg./cm.^{2}	Temperature (calculated)	Erosion cub. mm. per g.
Gunpowder, 75 per cent. saltpetre	2167	2910°	2·2
„ 78 „ „	1958	3513°	4·5
Nitro-guanidine	2019	907°	2·3
Nitro-cellulose	2276	2676°	6·4
Solenite (34 per cent. N/G)	2449	—	13·8
Dynamite (75 per cent. N/G)	2084	3161°	18·0
Cordite	2500	—	18·1
Nitro-mannite	2361	3429°	23·6
Ballistite (50 per cent. N/G)	2440	3384°	24·3
Blasting gelatine	2458	3545°	31·4

This clearly shows the influence of the temperature of the explosion gases. The lower the melting-point of the metal, the more it is eroded ; the following results were obtained by firing charges of 3·55 grains of ballistite, using plugs of different metals :

Platinum	59·1 cub. mm.
Platinum-iridium	74 „
Iron	68·2 „
Cannon steel	84·5 „
Chrome steel (3·5 per cent.)	98 „
Copper	98·8 „
Nickel steel (24 per cent.)	107 „
Cast iron	131 „
Silver	230·8 „
Bronze	279 „
Brass	326 „
Zinc	1018 „

It will be seen that the melting-point affects the erosion far more than the hardness of the metal. Similar experiments have been carried out in America,[1] where charges of smokeless powder were fired in an armour-piercing shell, closed with plugs of different metals, which were drilled with holes 3·97 mm. in diameter. The erosion was measured by the number of times the area of the orifice was enlarged :

Wrought iron	4·5 times.
Martin steel	4·5 „
3 per cent. tungsten steel	4·5 „

[1] *See S. S.*, 1907, p. 211.

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Martin steel with 3 per cent. tungsten	4·7 times
3½ per cent. nickel steel	5·0 ,,
20 per cent. nickel steel	5·9 ,,
Manganese bronze	23·0 ,,

The erosion is to be ascribed to the fusion of the surface of the metal, which is then swept away by the rush of gas. As regards the influence of pressure Vieille found that up to a pressure of 100 kg./cm.² the erosion was only slight; it increases very rapidly with rise of pressure from 900 to 2000 kg./cm.², and then remains practically constant from 2000 to 4000 kg.

Noble carried out an elaborate series of experiments with cordites specially manufactured with varying proportions of nitro-glycerine.[1] These were tested in the calorimetric bomb and also fired from the gun. The results are shown in Fig. 56. It will be seen that when the percentage of nitro-glycerine is increased from 10 to 60 per cent., the quantity of heat increased 60 per cent., but the erosion was greater by nearly 500 per cent.

When only small charges are used, the erosion is not very severe, for both the temperature and pressure in the chamber are much lower. It is largely for this reason that practice with large guns is mostly carried out with reduced charges. It is reckoned that the wear of the gun due to a proof round is equal to that of two full charges, and that a full charge of powder is equivalent to four ¾-charges or sixteen ½-charges or sixteen blank charges. One round of cordite Mk.I is equivalent to several of cordite M.D. producing the same ballistics. It is in large ordnance, firing very heavy charges of powder in order to obtain a high muzzle velocity, that the erosion is most severe; in smaller guns it is comparatively trifling. By properly proportioning the chamber and the length of the gun, and making the powder of the right size and shape, the erosion can be reduced somewhat, but naval guns of large size require re-lining after they have fired a few hundred full charges.

With smokeless powder the erosion mostly consists in washing the surface of the metal smoothly away. With high charges of black powder, which generated temperatures of the same order, the metal was scored into deep ruts, and this has been ascribed to the mechanical action of the solid particles in the products of explosion. With smokeless powder there is some scoring, but not nearly so much.

Erosion is most severe, not in the powder chamber, but just in front of it, where the powder gases rush past between the copper band of the projectile and the bore of the gun. Further down the bore the wear is much less, as the pressures are less, the copper bands fit the rifling better, and the projectile is travelling so rapidly, that the escapes of gas have little time to do harm.

The inner tubes of guns also occasionally split. This is apparently caused by the alternate heating and cooling of the inner surface of the metal combined

[1] *Artillery and Explosives*, p. 534.

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with the compression to which it is subjected. The result is that the surface layer of metal is in a state of tension.

Yarnell has shown that just as nitro-glycerine powders cause more erosion than those that only contain nitro-cellulose, so nitro-cellulose powders of

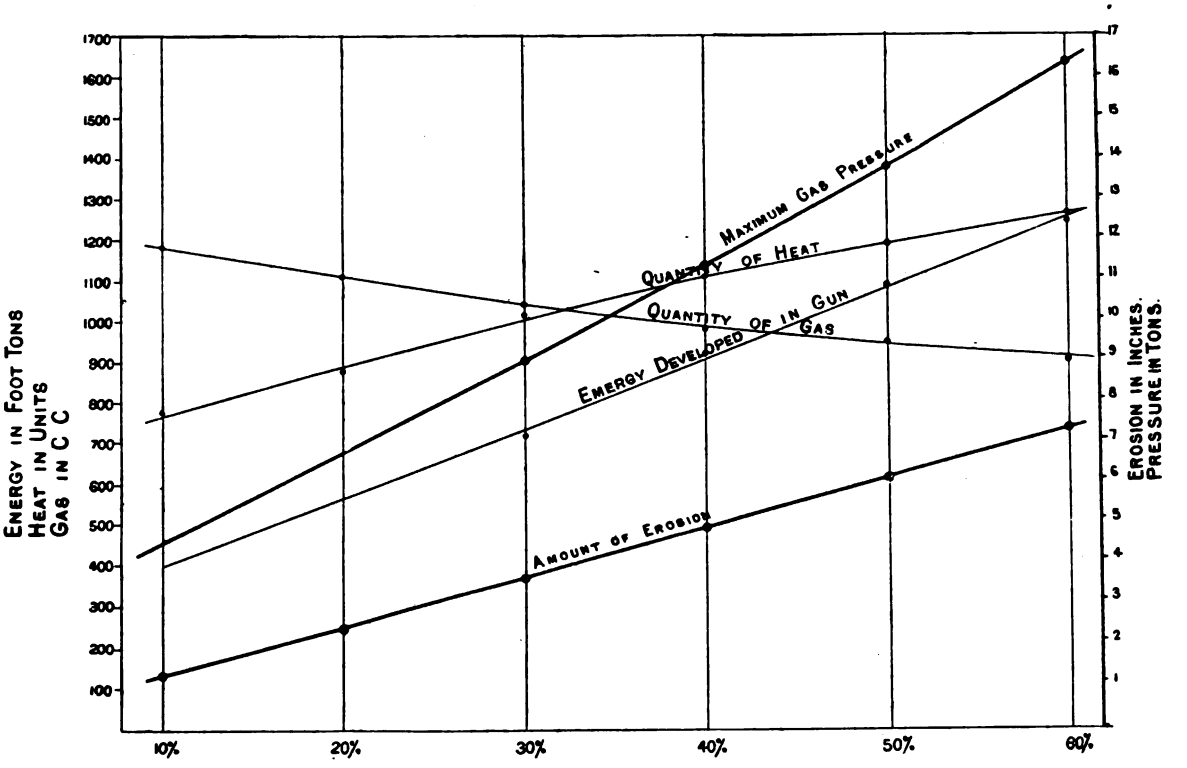

FIG. 56. Noble's Erosion Experiments

high nitration are worse in this respect than those of low nitration, in spite of the fact that a smaller charge is required.[1] Like Vieille he found that the erosion is practically independent of the pressure if it exceed 2000 atmospheres. Yarnell also tried the effect of adding considerable quantities of water or paraffin to the charge. The erosion was greatly reduced thereby, and the pressures were increased. Such additions have been advocated frequently, but apart from the difficulty of carrying them out under war conditions, the presence of cooling material in the lump, so to speak, must render the ballistics uneven. Any addition should be incorporated with the powder during manufacture. The mineral jelly in cordite reduces the tempera-

[1] *Journ. Amer. Soc. Naval Engineers*, May 1910 ; *S.S.*, 1911, p. 193.

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ture of the products several hundred degrees, and in fact cordite M.D. has a temperature of explosion, which is but little higher than that of some nitro-cellulose powders. An addition such as this does not diminish the ballistic efficiency of the powder to any great extent, because the reduction of temperature is partly compensated by the increase in the volume of gas formed.

Vieille (*loc. cit.*) showed the effect of adding nitro-guanidine to powders :

	Erosion per gramme		
	Nitro-cellulose Powder	Cordite	Ballistite
Alone	6·4	18·1	24·3
With 30 per cent. nitro-guanidine . .	5·45	13·0	14·2
„ 50 „ „ . .	3·44	8·44	7·8

The difficulty is to find a substance that can be incorporated with the powder in sufficient quantity without affecting injuriously any of its qualities. Nitro-guanidine, for instance, makes it brittle.[1]

Back-flash. With a low temperature of explosion is always associated a low percentage of oxygen in the powder, and consequently a large proportion of carbon monoxide in the products, and there is always a danger that this gas may catch fire when the breech is opened after firing a shot. In France, where nitro-cellulose powder only is used, a number of disasters have been caused by such flames emerging, and setting light to cartridges in the turret, or standing near the gun. Similar accidents have occurred in the United States, where also nitro-cellulose powders are employed exclusively.

Muzzle flame. When cannon are fired, flames appear at the muzzle due to the ignition of the combustible gaseous products. This is objectionable, because at night it reveals the position of the guns. The flame can be diminished or even abolished by adding a few per cent. of sodium resinate or other sodium or potassium salt,[2] but the quantity of smoke is thereby greatly increased and this will reveal the position by day, and will obstruct the gunners.

[1] Bravetta, *S.S.*, 1912, p. 493.

[2] *See* Schildermann, *S.S*, 1913, p. 126.

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CHAPTER XX

SMOKELESS SHOT-GUN POWDERS—BLANK POWDERS

Shot-gun powders : Condensed powders : Bulk powders : Ingredients : Manufacture of bulk powders : American method : 33-grain powders : 30-grain powders : French powders : German powders : American powders : Austrian powders : Requirements : Blank powders

THE shot-gun is distinguished from the rifle not only in not having a rifled bore, but also in being generally of considerably greater calibre. To produce a weapon easy to handle it is necessary to make the forward portion of the barrel very light, and therefore there must be but little pressure except near the breech. The distribution of the shot in a uniform manner, *i.e.* the formation of a good pattern, seems to require that comparatively little pressure be exerted on the shot in the forward portion of the barrel. For these reasons a shot-gun powder must burn much more rapidly than a rifle powder, and therefore there must be more surface exposed. These powders are of two kinds : the " condensed " and " bulk " types.

Condensed powders.

In the condensed powders the nitro-cellulose is completely gelatinized ; they are made in much the same way as rifle powders, but are formed into quite small grains or very thin flakes. Cannonite, Shot-gun Rifleite and Sporting Ballistite are of this type, but the first two of these are no longer manufactured ; their composition is given in the Table on p. 252. Canonnite was made in the form of small graphited grains ; the process of manufacture was described by Sanford in the first edition of his *Nitro-Explosives*, 1896, p. 182. Shot-gun Rifleite was in the form of thin flakes ; Sporting Ballistite is also a flake powder. The advantages claimed for these powders are that they leave very little solid residue when burnt, and are consequently free from smoke and " blow-back," and leave but little fouling in the bore, that they are not much affected by exposure to moist air, are very quick and give little recoil. On the other hand, they require special cartridge cases with a cone of pasteboard filling up part of the base, because their density is so high. In consequence of the small space occupied by the powder charge very slight variations in the strength of the cap and other conditions produce great variations in the pressures generated, and the gun may therefore be strained dangerously, and difficulties are sometimes experienced in extracting the

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cartridge cases. These powders are also more difficult to manufacture than those of the bulk type.

Bulk powders. Bulk powders are so made that the charge for a 12-bore gun occupies the same space in the cartridge as the standard charge of 3 drams of black powder. The first successful smokeless powder was that of Captain E. Schultze, of the Prussian Artillery, who made it from nitrated wood.[1] This was first cut into thin veneers, from which small cylinders were punched, and then it was purified by boiling with soda, bleaching and washing. After nitration the nitro-lignin was boiled with soda, and washed with cold water, and afterwards impregnated with the nitrates of barium and potassium. In the course of time various modifications have been made in the process of manufacture. The wood fibre now used is thoroughly purified by drastic chemical treatment, and is formed into grains by manipulation with solvents after nitration. The treatment with solvent also hardens the grains and makes them more waterproof. For further information about the early development of Schultze powder *see ante*, p. 37 , also Guttmann, *Progress*, p. 38 and Appendices, and Griffith's Patents 3,294 of 1877, and 11,808 of 1884. Most of the other powder manufacturers use nitro-cotton instead of nitro-lignin, but the Schultze Company have adhered to wood fibre, as they consider that a powder made with it is less sensitive to variations of loading, and gives more satisfactory results under adverse climatic conditions. The lower cost of wood cellulose as compared with cotton is offset by the fact that the yield of nitro-cellulose is lower, and there is consequently a waste of nitric acid.

Ingredients. Bulk powders frequently contain a small proportion of substances, such as vaseline or paraffin wax, which serve to moderate the action. Starch also is sometimes used ; it helps to hold the grains together. Camphor is somewhat objectionable, as it is volatile and escapes on long storage. The mono- and dinitro-derivatives of benzene and toluene are present in some powders ; they have the property of assisting the gelatinization of the fibres. Other materials that are added sometimes are lamp-black, wood meal, various gums and potassium ferricyanide. In order to complete the oxidation of such added organic matters, and also to make the rate of burning more uniform, nitrates of barium and potassium are added : the barium salt has the advantage that it produces comparatively little smoke and is not hygroscopic. On the other hand, it leaves a residue in the gun, which is difficult to remove. Therefore it is customary to use a considerable percentage of barium nitrate together with a small proportion of potassium nitrate. A small quantity of aniline dye is also added in many cases to colour the powder. Other powders are coated with graphite, which renders them less liable to become ignited by electrification, although there is little danger of this in powders that contain mineral salts. Graphiting also retards the ignition of the powder and so acts

[1] *See* Eng. Pat. 900 of 1864.

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as a moderating agent. The nitro-cellulose used generally contains 12·5 to 12·8 per cent. nitrogen, and is partially soluble in ether-alcohol. The addition of calcium carbonate improves the stability of the powder by neutralizing any acid that is given off, but it should be very intimately mixed with the nitro-cellulose, and such intimate contact is best produced by precipitating the carbonate in the fibres by using hard water for the boiling of the nitro-cellulose.

Manufacture of bulk powders.

The incorporation of the ingredients is in many cases performed under edge-runners similar to those used for the milling of black powder. The wet nitro-cellulose, containing some 40 per cent. of water, is roughly mixed with the other ingredients, and these are ground together in the mill, water being added from time to time to keep the mixture moist. The duration of the milling and the amount of water are regulated according to the gravimetric density required in the finished product. The longer the milling and the higher the proportion of water, the greater the gravimetric density. The material is then passed through a sieve with meshes somewhat larger than the finished grain is to be. The moist grains thus formed are then dried in a stove by means of a current of hot air, the powder being spread on trays to a depth of not more than 3 inches. When dry the material should be allowed to cool down in the stove before it is moved. The dust and large lumps are then removed by passing the powder through slope reels.

FIG. 57. English Bulk Powder
(Thörner, *S.S.*, 1907, p. 424)

The next operation is the important one of hardening the grain by treating it with solvent. This is frequently done by spraying it with the solvent inside a drum, which can be closed hermetically and rotated about its axis. After a few minutes rotation the grains are thoroughly moist. The powder is then allowed to steep for some time either in the same vessel or another one, and then it is dried. The preliminary drying may be carried out in a solvent recovery plant consisting of a rotating drum provided with a steam jacket and a hollow axle, which is connected through a condensing coil with a vacuum pump. The coil, pump, etc., are placed in a separate compartment from the drying drum, which is isolated by means of a wall having no openings, in order to minimize the danger of fire. A considerable proportion of the solvent is recovered in this way, and after redistillation may be used again, but in order to obtain a satisfactory recovery it is necessary to cool the coil by means of refrigerated brine to a temperature considerably below the freezing-

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point of water. The drum is fitted with ribs inside to prevent the powder simply sliding round in a cake. The exit is covered with wire gauze and cotton wool to prevent dust being drawn into the condenser. The man-hole lid fits air-tight, and can be held on by means of thumb-screws, but during the drying these screws are removed so that the lid is held on by the vacuum only. If pressure arises at any time during the drying the lid will at once fall off and relieve the pressure. The temperature of the powder should never exceed about 50° C. (122° F.). The powder as it comes from the drums contains 3 or 4 per cent. of water and solvent. The drying is completed on trays in a drying stove. When dry it is sifted so as to remove the grains that are too large or too small: these are added in small proportion to a further charge in the milling operation. Finally, the powder is tested for stability and ballistics, and carefully blended with other batches so as to obtain the standard results. But before the final tests are made the powder should be kept for a month or two in order that it may take up the normal amount of moisture. In case of necessity it can be "aged" artificially by exposing it for a few hours to a hot moist atmosphere, but natural ageing is more satisfactory.

This scheme of manufacture has been varied in many ways. The incorporation, for instance, can be performed in drums with lignum vitæ balls. The mass can then be pressed and broken up into grains of the desired size much as is done with black powder. Granulation can also be effected by sprinkling the powdery material with water and then rotating in a drum. Various solvents have been used by different powder-makers: mixtures of ether and alcohol, acetone and alcohol, and acetone and ether have been employed. Ether is very volatile and consequently the losses are considerable. Ether-alcohol only partially gelatinizes the nitro-cellulose unless the degree of nitration is low. Benzol is sometimes added to moderate the action.

American method.

According to C. E. Munroe,[1] the following method is adopted in America for the production of shot-gun powder with fibres entirely gelatinized. The manufacture is conducted in a stationary still of copper about 5 feet in diameter with conical ends. A shaft extends downwards through a stuffing box in the top to a point near the bottom. At intervals of about 8 inches horizontal arms are attached to this shaft; they extend almost to the walls on either side. Five of these are square in cross-section and about 1 inch thick, but the sixth bar, which is the top one, is flattened out so as to form paddles which slant in the direction of motion of the shaft in such a way as to smooth down the surface of the contents of the still. The height from the bottom to the top stirrer blades is about 6 feet 3 inches.

The orifice at the bottom of the still having first been closed, the vertical shaft is set in rotation at a speed sufficient to maintain the particles of gun-cotton in mechanical suspension in the solution: this rotation is maintained

[1] *U.S. Census Bull.*, 92, 1908, p. 84.

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during the whole of the process. Water in which 5 per cent. of barium nitrate and 2 per cent. of potassium nitrate have been dissolved is then pumped into the still, and finely pulped gun-cotton is thrown in through an opening in the upper part. In all 450 lb. of fresh gun-cotton and some 250 lb. of dust and fine grains from previous granulations are introduced. More of the nitrate solution is pumped in, and finally the opening is closed, and an emulsion is pumped in consisting of 25 to 50 per cent. amyl-acetate in nitrate solution. The surface of the liquid should now be up to the top stirrer blades.

The material now begins to granulate, and the progress of the granulation is observed by withdrawing a little of the mixture through a small orifice near the bottom of the still. When granulation has been effected throughout the mass, which is within five minutes of the time when the introduction of the emulsion into the still was commenced, steam is turned into the jacket surrounding the lower portion of the still. Heating is continued for five or six hours, by which time practically all the amyl-acetate has been distilled over together with some of the water. This is condensed and the amyl-acetate is separated. A gate valve in the bottom of the still is now opened, and the mixture of water and granulated powder is drawn off into a draining tank. After draining it is dried, sized, blended and packed. The strength and amount of the emulsion used depend upon the amount and quality of the gun-cotton; the best proportions are ascertained by experience. The finished powder is coloured to suit the taste of customers.

The older powders, Schultze and Amberite, are 42-grain powders, that is to say the charge required for an ordinary 12-bore cartridge is 42 grains, and this quantity occupies the same space in the cartridge as 3 drams of black sporting powder. The powders named are still used extensively, but there is a growing demand for powders of which smaller charges are required, the principal advantage of which is that they give a decidedly lighter recoil, for the powder products are ejected from the muzzle of the gun with higher velocity than the shot. It is also claimed that they are quicker. Reduction of charge is effected by using a nitro-cellulose of higher nitrogen content, and reducing the proportion of the other constituents. These changes increase the rate of burning, so in order to prevent the production of dangerous pressures in the gun it is necessary to gelatinize the nitro-cellulose more completely.

Thirty-three-grain powders.

A 33-grain powder can be made in much the same manner as is described above, except that after the grains have been formed and hardened a portion of the nitrates is washed out by steeping the materials in water. A well-known 33-grain powder of English manufacture is Smokeless Diamond; Henrite is another of this class: both these are in the form of black grains. E.C. No. 3 is a 33-grain powder too; it is coloured yellow with aurine.

Thirty-grain powder.

By taking a further step in the same direction the charge can be reduced to as little as 30 grains. The nitro-cellulose is mixed with a small proportion

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of " reducers " and several times its weight of barium and potassium nitrates. It is then incorporated in a Werner and Pfleiderer machine with sufficient acetone or other suitable solvent to gelatinize it entirely. The dough is then formed into small cubes or prisms by processes similar to those employed for rifle powders, and after drying, the mineral nitrates are dissolved out as completely as possible with warm water. Only about 5 per cent. are left in. Schultze Cube Powder is an instance of a 30-grain powder produced by a process of manufacture of this sort.

	Imperial Schultze	Amberite	S.S.	E.C.	Schultze	Kynoch's Smokeless	Cannonite	Shot-gun Rifleite	Walsrode	Sporting Ballistite
Nitro-glycerine	—	—	—	—	—	—	—	—	—	37·6
Nitro-cotton	—	71·0	59·2	79·0	—	52·1	86·4	94·0	98·6	62·3
Nitro-lignin	80·1	—	—	—	62·1	—	—	—	—	—
Dinitro-toluene	—	—	15·7	—	—	19·5	—	3·5	—	—
Potassium nitrate	—	1·2	1·3	4·5	1·8	1·4	—	—	—	—
Barium nitrate	10·2	18·6	17·0	7·5	26·1	22·2	5·7	—	—	—
Camphor	—	—	—	4·1	—	—	—	—	—	—
Wood-meal	—	1·4	5·2	3·8	—	2·7	—	—	—	—
Vaseline	7·9	5·8	—	—	4·9	—	2·9	—	—	—
Starch	—	—	—	—	3·5	—	—	—	—	—
Lamp-black	—	—	—	—	—	—	1·3	—	—	—
Pot. ferricyanide	—	—	—	—	—	—	2·4	—	—	—
Calcium carbonate	—	—	0·6	—	—	—	—	—	—	—
Ash	—	—	—	—	—	0·9	—	0·9	—	—
Volatile matter	1·8	2·0	1·0	1·1	1·6	1·2	1·3	1·6	1·4	0·1
Calories per g.	742	745	755	762	786	807	845	896	1014	1286
Permanent gas, c.c. per g.	763	635	695	718	576	600	725	705	669	591
Aq. vapour, c.c. per g.	152	156	131	158	160	126	146	169	206	234
Total vol. gas N.T.P.	915	791	816	876	736	726	871	874	875	825
Compn. permanent gas p.c.:										
CO_2	8·9	12·0	11·8	11·9	15·5	14·8	14·6	19·0	21·3	32·2
CO	52·7	50·0	51·3	52·1	46·7	49·5	49·9	45·3	48·2	37·1
CH_4	1·0	0·4	0·8	0·5	0·8	0·7	0·6	0·8	0·4	0·4
H_2	27·0	25·5	23·7	23·9	23·0	18·8	22·2	21·5	10·1	10·1
N_2	10·4	12·1	12·4	11·6	14·0	16·2	12·7	13·4	14·8	20·2
Relative temperature	106	123	135	136	137	139	150	160	161	204

The above Table published in 1904 by Macnab and Leighton,[1] gives the composition of the principal shot-gun powders at that time in use in England, together with the amount of heat generated in the calorimetric bomb and the

[1] *J.S.C.I.*, 1904, p. 298.

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composition of the products of explosion. Of these, Shot-gun Rifleite, Sporting Ballistite and Cannonite were condensed powders. S. S., Shot-gun Rifleite and Cannonite are no longer made.

Sporting ballistite is made in much the same manner as rifle ballistite, except that after the sheets have been rolled out, acetone is added and the rolling is repeated, so that the finished sheets are only 0·065 inch thick and look like oiled silk. These are cut into small flakes. The normal charge of a 12-bore cartridge is only 26 grains.

In France the manufacture of sporting powders forms part of the State monopoly of explosives. The following Table gives the composition of the powders made : French powders.

Poudre	S.	J.	M.	T.
Nitro-cotton	65	83	71	100
Barium nitrate	29	—	20	—
Potassium nitrate	6	—	5	—
Am. bichromate	—	14	—	—
Potassium bichromate	—	3	—	—
Camphor	—	—	3	—
Binding material	—	—	1	—
Moisture	2	3	—	1·5
Price Fr.	28	28	30	32

The following details of manufacture are given in *P. et S.*, 1912, xvi. pp. 99, 100 :

Poudre S. The materials are mixed under light edge-runners, dried, incorporated with ether(-alcohol ?) like Poudre B. The dough, which is not very coherent, is formed into grains by simply passing it through a sieve. The grains are dried, sifted, if necessary hardened with ether(-alcohol) and again dried and sifted.

Poudre J. This is made in the same way as Poudre B. The strips of powder are plunged frequently into water for the sake of safety.

Poudre M. The constituents are incorporated together with the aid of ether(-alcohol) as in the case of Poudre B. The mass is then triturated under light edge-runners, passed through a sieve, which divides it into grains, polished in small wooden barrels, and dried. The dust is sifted from the dry grains, which are then hardened in large barrels with a spray of ether-alcohol containing collodion and camphor, which forms a skin on the surface. Then the material is dried and sifted. The powder is coloured yellow with auramine.

Poudre T. The nitro-cotton is gelatinized with acetic ether and acetone.

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The dough is pressed into strips, which are then rolled out to a thickness of about 0·1 mm.

Dissatisfaction has been expressed with regard to these French sporting powders, and in 1908 the Minister of War instructed the Committee of the service of "Poudres et Salpêtres" to compare them with foreign powders. Comparative experiments were carried out with Poudre T, Sporting Ballistite and the German condensed powder Mullerite, and it was admitted that the results from the French powder were more irregular. The sales of Poudre T amounted to 22,358 kg. in 1909 and 20,123 in 1910.

German powders. The following are some of the principal German shot-gun powders :

Rottweil. Square flakes with metallic lustre. Charge 2·22 g. (34·3 grains).

Saxonia. Square flakes, bluish green. Charge 1·90 g. (29·4 grains).

Mullerite. Thin square flakes, green. Charge about 35 grains. Contains no inorganic salts.

Walsrode. Small grains, greyish-white and greyish-green, mixed. Charge 2·27 g. (35·0 grains).

Adler-Marke. Small cylinders, grey. Charge 2·00 g. (30·9 grains).

Wolf-Marke. Grains, white and yellow, mixed.

Fasan (Pheasant). Grains, greyish-yellow. Charge 2·65 g. (40·9 grains).

Tiger. Grains, blue-black. No lustre. Charge 2·73 g. (42·1 grains).

American powders. The American explosives industry is largely in the hands of the E. I. du Pont de Nemours Powder Co., who make the following :

Condensed powders : Infallible and Sporting Ballistite.

Bulk powders : Du Pont Smokeless, E. C. Improved, New Schultze, Empire and Lesmok.

Austrian. In Austria there is a State monopoly of explosives. Information about the sporting powders is given in *S.S.*, 1909, p. 413, but their quality has been decried.[1]

Requirements. The requirements of a good shot-gun powder are : (*a*) That it shall be reliable and constant in its qualities : this is as important as in the case of other gunpowders, and somewhat more difficult to attain ; great care in manufacture and thorough blending are necessary. (*b*) It should burn cleanly, leaving little residue in the gun, and what residue there is, should be alkaline in reaction and easily removed. (*c*) It should give good results, even when loaded into cheap cartridge cases, with indifferent wadding and light shot charges. (*d*) It should be quick in ignition : a delay of a few thousandths of a second in the time that elapses between pulling the trigger and the shot leaving the muzzle makes a considerable difference in the accuracy of the shooting ; smokeless powders burn considerably faster than black. (*e*) It

[1] *See S.S.*, 1910, p. 320.

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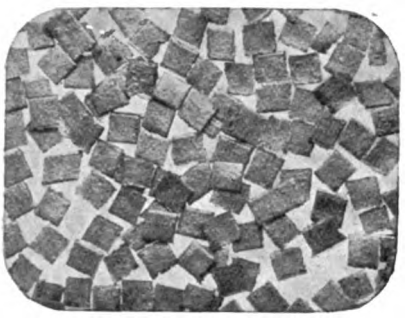
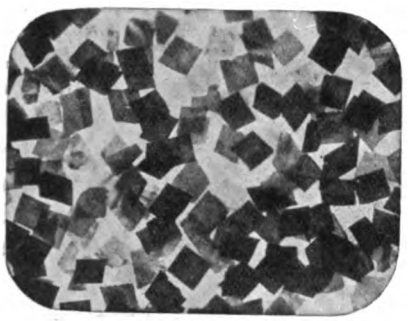
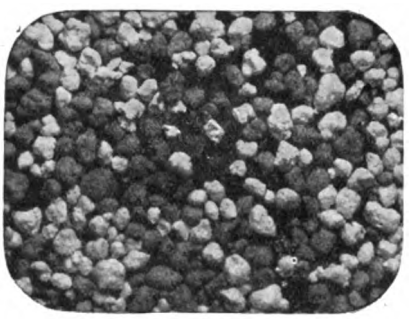


Rottweil

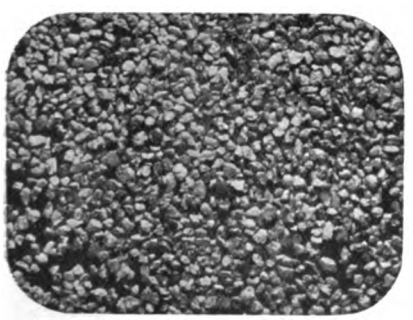
Adler-Marke



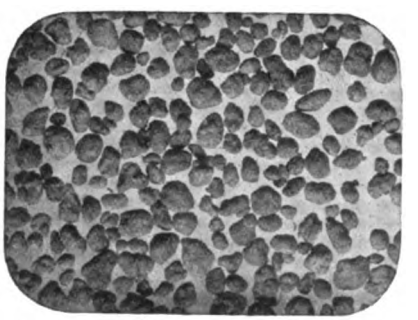
Saxonia



Wolf-Marke



Walsrode



Fasan

FIG. 58. German Smokeless Shot-Gun Powders (Thörner, *S.S.*, 1907, p. 423)

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should not be greatly affected by exposure to hot or moist air. (*f*) It should occupy about the same space as the equivalent charge of black powder: in the manufacture of cartridges the charges are measured and not weighed, and if the powder be very dense, there is considerably greater danger of an extra large charge being introduced accidentally.

Blank powder. Blank powders are used for firing time and other signals, for manœuvres and displays, such as *feux de joie;* in all cases in fact where it is required to make the noise of firing without ejecting a projectile. Difficulty is caused by the fact that there is no projectile to offer resistance to the expansion of the powder gases: consequently as soon as the envelope containing the powder is burst the pressure falls almost to nothing. With black powder this does not matter very much, as the rate of burning is not affected to the same extent by the pressure; gunpowder can be used indeed for this purpose which is not good enough for ordinary cartridges. The rate of burning of nitro-powder on the other hand, is greatly affected by the pressure: there is danger therefore if the envelope offer a little too much resistance or the primer be too strong, that dangerous pressures may be set up in the gun: and if the resistance or the ignition be too weak the report will be insufficiently loud.

As in the case of shot-gun powders the rapidity of burning is attained either by using a partially gelatinized material, or a completely gelatinized one in a fine state of division. In the British service the small-arm blank cartridges have a charge of 20 grains of cordite size 20 S.C. S.C. stands for "sliced," and this powder is made by passing strands of cordite about 0·20 inches in diameter through a machine, in which it is cut transversely by rapidly rotating knives into small discs having a thickness of about 0·0055 inch. For ordnance, however, black powder is still used generally. In France a special powder is manufactured known as Poudre EF, which is made of nitro-cotton and binding material in much the same way as Poudre M.[1] In Spain a nitro-cellulose flake powder is used for small-arm blank ammunition.[2]

[1] *P. et S.*, 16, 1912, p. 100.

[2] *S.S.*, 1908, p. 284.

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CHAPTER XXI

SOLVENTS

Solvents available : Ether-alcohol : Solution of colloids : Manufacture of acetone : Permanganate test : Impurities : Acetone from starch : Recovery of solvents : Acetone recovery : Volatility of nitro-glycerine : Vapour explosions : Toxicity of vapours

Solvents available.

In the powders first introduced, Schultze, E.C., Poudre B, the solvent used was a mixture of ether and alcohol, which had been employed in making collodion solutions for many years. When the English Government introduced cordite in 1888, they adopted a solvent, which had been but little used previously except in the laboratory, namely, acetone. This possesses the advantage that it can dissolve gun-cotton even of the highest degree of nitration.

In the lacquer and celluloid industries various solvents for nitro-cellulose are used in order to obtain different specific effects. Amyl-acetate especially is much employed in the preparation of lacquers. Its great value lies in the fact that it boils at a high temperature; consequently the surface does not become cooled by rapid evaporation, and so condense water from the air. Moreover, from a mixture of amyl-acetate and water the latter evaporates proportionally much faster than the former. Consequently the solution of nitro-cellulose gradually sets to a clear solid film, as the amyl-acetate evaporates, whereas if only very volatile solvents such as ether and alcohol are used, water accumulates more and more, until it precipitates the nitro-cellulose in an opaque form.

In the manufacture of military and rifle powders there are not many different solvents used. If gun-cotton with some 13 per cent. of nitrogen be the base, either acetone or ethyl-acetate is used, generally the former. If a "soluble" nitro-cotton be the base, ether-alcohol is usually employed. In Poudre B amyl-alcohol is added for a purpose somewhat similar to that for which amyl-acetate is used in lacquers. For sporting shot-gun powders a somewhat wider range of solvents is in use, and they are often mixed in order to produce certain specific effects.

The subject of the solubilities of nitro-celluloses in the various simple and mixed solvents has never been thoroughly investigated, although it is of

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considerable practical and theoretical importance. De Mosenthal gave a long list of solvents that have been mentioned in patent specifications,[1] but in the absence of information as to the sort of nitro-cotton or the conditions under which it is dissolved, the list is not of great value.

Gun-cotton containing about 13 per cent. nitrogen only dissolves to a small extent in ether-alcohol, but is totally dissolved or gelatinized by acetone and other ketones, by aldehydes such as benzaldehyde and furfurol, by esters such as ethyl-acetate (acetic ether), by acid anhydrides such as acetic anhydride, and by some nitro-compounds such as nitro-toluene. On the other hand, it is not dissolved by nitro-benzene, nitro-phenol, or organic acids such as acetic or formic. Excepting nitro-toluene all the above solvents for gun-cotton contain the group :CO connected with two other radicles other than hydroxyl, —OH.

Ether-alcohol.

"Soluble" nitro-celluloses are distinguished from gun-cotton by the fact that they are soluble in a mixture of ether and alcohol: of any ether and any alcohol; whereas they are practically insoluble in the ether alone and only dissolve with difficulty in absolute alcohol. From determinations of the viscosity of mixtures of various alcohols and ethers F. Baker[2] finds evidence of the formation of compound molecules such as C_2H_6O, $C_4H_{10}O$, and it is these apparently, which have the property of dissolving the nitro-cellulose; but Bingham has pointed out that the evidence is not conclusive.[3] An alternative theory is that the ether only plays a passive part in causing the associated molecules of alcohol (R.OH)n to split up into simple molecules R.OH, which latter dissolve the substance. But this theory is inconsistent with some of the facts: other liquids which are known not to combine with the alcohol, such as benzene, cannot be substituted for ether; then again the most associated alcohols, methyl- and ethyl-alcohols, have the greatest solvent powers when mixed with ether; also the solvent power of a mixture of ether and alcohol is increased by reduction of temperature.[4] All these facts are consistent with the theory that it is the compound molecules of ether-alcohol that have the solvent power, but not that this property resides in the unassociated molecules of alcohol. The solubility in various mixtures has been investigated by Stepanow,[5] who found that the maximum solubility is obtained when the proportion of ether to alcohol is 3 : 2, *i.e.* when the two liquids are mixed in about equi-molecular proportions. The addition of solvents such as acetone or ethyl-acetate, increases the solubility in ether-alcohol, but indifferent substances such as benzene, toluene, pyridine, phenol, chloroform

[1] *J.S.C.I.*, 1904, p. 295.

[2] *J.C.S.*, 101, 1912, p. 1409.

[3] *J.C.S.*, 103, 1913, 964.

[4] W. Macnab succeeded in dissolving highly nitrated "insoluble" gun-cotton in ether-alcohol by reducing the temperature to that of solid carbon dioxide.

[5] *S.S.*, 1907, p. 43.

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diminish the solubility, the diminution being proportional to the quantity added. Other substances, such as water and acids, also affect the solubility, but not proportionally.

Soluble nitro-cellulose or collodion cotton is also dissolved by nitro-glycerine, acetic acid, etc. In the celluloid industry use is made of the solvent power of camphor, and there are a number of other substances, solid at the ordinary temperature, which have the same property: the dissolution is greatly promoted by the addition of alcohol. It has been found by Bernadou that at a low temperature nitro-cellulose is dissolved by ether alone.

Lunge and Bebie [1] found that a nitro-cotton containing about 11 per cent. N was soluble in absolute alcohol, but insoluble in 95 per cent. alcohol. Ennea-nitro-cellulose (12 per cent. N) only dissolved to the extent of 70 per cent. in absolute alcohol, but a deka-nitro-cellulose (12·75 per cent. N), although completely soluble in ether-alcohol, only dissolved in absolute alcohol to the extent of 1·3 per cent. With a nitro-cotton containing 11·5 per cent. N the following results were obtained with the ether and alcohol in varying proportions:

Ether : Alcohol		Ether : Alcohol	
1 : 3	Dissolves readily	—	
1 : 6	Less readily, 93 per cent. after treating twice.	6 : 1	Dissolves readily.
—		9 : 1	Less readily, 95 per cent.
1 : 12	More readily, 96 per cent. after treating once.	12 : 1	92·1 per cent. dissolved.
1 : 24	95·6 per cent.	27 : 1	7·3 „ „

Similar experiments have been carried out by A. Matteoschat with a nitro-cellulose of medium solubility containing 12·95 per cent. nitrogen.[2] The solvents used consisted of pure ether and pure alcohol containing varying percentages of water mixed in different proportions. To prevent surface gelatinization of the nitro-cellulose the alcohol was added first and then the ether. The following were the solubilities found:

	Strength of Alcohol by Volume			
Ether : Alcohol	99·5%	95%	90%	80%
1 : 2	32·4	—	—	—
1 : 1	52·3	42·3	28·7	14·2
2 : 1	40·5	52·4	53·9	45·0
3 : 1	25·0	42·4	53·0	57·5

Colloidal solution.

The dissolution of a colloidal substance, such as nitro-cellulose, differs fundamentally from that of crystalline substances, such as sugars or the ordinary mineral salts. The surface material does not pass into the liquid and diffuse away, leaving the remainder of the solid unaffected. On the

[1] *Ang.*, 1901, p. 537. [2] *S.S.*, 1914, p. 105.

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contrary, it is the liquid which passes into the colloidal solid, causing it to swell gradually. As it does so, the solid becomes softer and softer until finally it is liquid and can be mixed with the bulk of the solvent.

Manufacture of acetone.

Acetone is made by the dry distillation of acetate of lime, which in turn is a product of the dry distillation of wood. Beech, birch and the American maple are the trees most concerned, as they yield comparatively large quantities of acetic acid on distillation. Coniferous trees, the fir and pine, on the other hand yield little acetic acid ; the most valuable product from their distillation is turpentine. Even from the most suitable woods the yield of acetone is small : only 8 to 10·5 parts of acetate of lime of 80 per cent. strength are obtained from 100 of dry wood, and this in turn only yields about 20 per cent. of acetone. Moreover, fresh felled beech or maple contains about 40 per cent. of moisture. Consequently it requires from 80 to 100 tons of wood to produce 1 ton of acetone, and the manufacture is dependent on the supply of very large quantities of wood. Attempts have been made to manufacture acetate of lime and other products by the distillation of sawdust, waste wood and other woody materials, but most of these undertakings have hitherto proved unremunerative. The charcoal obtained from these waste materials is generally of little value, and the yield of acetate and wood spirit is considerably less than from good new wood.

" Grignon," the residuum left after pressing the oil from olives, is now distilled on a large scale in Spain. It yields about 4 per cent. of acetate of lime and 1·2 per cent. of crude wood spirit. Other waste products consisting principally of cellulose and lignin might be utilized similarly ; coffee husks, for instance, and the wood from which tannin and dye extracts have been made, such as quebracho chips. In course of time these materials will no doubt be utilized, but only where very large supplies of them are available.

The first necessity of a wood distillation plant is a plentiful supply of wood, the second is a ready market for the charcoal. As a rule a plant will not be remunerative, unless the selling price of the charcoal covers the cost of the wood used.[1] The value of the by-products, acetate, wood spirit and tar, then only has to provide the cost of working, interest and profit.

Charcoal, although it weighs only about one-third as much as the original wood, occupies nearly as much space. Moreover, it is decidedly brittle, and if it has to be transported very far by road or rail, a large proportion of it is converted into powder, which has a comparatively small value. Therefore a wood distillation plant should be situated where there is a plentiful supply of suitable wood, a ready market for the charcoal, and good means of communication. The by-products, acetate, crude wood spirit and tar, are comparatively light and can be transported over considerable distances to a central chemical factory to be worked up.

[1] Klar, *Holzverkohlung*, second ed., p. 62.

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These conditions are present in many parts of India. Nevertheless charcoal is still produced there in small kilns and the valuable by-products are allowed to escape. The reason is that technical knowledge is deficient, and capital is not available through want of enterprise. Most of the acetate of lime and acetone are manufactured in the United States,[1] but there are also large plants for their production in Hungary, Sweden, Russia, and Canada.

By the destructive distillation of wood three different classes of products are obtained: solid, liquid and gaseous. The solid, charcoal, remains in the kiln or oven; the liquid, crude pyroligneous acid, is recovered from the mixture of gas and vapour by means of a suitable condenser; and the gases pass on and may be used either for heating, or to drive a gas-engine, but a further quantity of methyl-alcohol and acetic acid can first be recovered from them by scrubbing with water in a tower. By distillation and treatment with milk of lime the crude pyroligneous acid is further separated into tar, acetate of lime and commercial wood spirit.

The acetate of lime is not as a rule worked up further at the carbonization works, but is sent to a chemical factory where large quantities are collected and worked up into acetone, acetic acid, and various acetates and derivatives of acetic acid. There are two varieties of commercial acetate of lime, brown and grey, which differ from one another in that the grey acetate has had the tar removed as far as practicable, and the brown has not. Brown acetate is not made now on a very large scale, as it gives very bad yields of acetone and acetic acid. Grey acetate generally contains 80 to 82 per cent. of calcium acetate as determined by analysis, and 4 to 7 per cent. of water, the remainder being made up of various impurities. Of the 80 to 82 per cent., however, several per cent. consist of formate, propionate and salts of other organic acids.

The conversion into acetone is effected by simply heating the acetate at a temperature of about 300° C., when the following reaction takes place: $Ca(CO_2CH_3)_2 = CaCO_3 + CH_3CO.CH_3$, but the other organic calcium salts react in a similar manner: formic acid yields aldehydes, propionic acid methyl-ethyl-ketone and diethyl-ketone, and the higher homologues the corresponding higher ketones.

The distillation of the acetate of lime is usually carried out in a shallow circular retort heated by direct fire. Fig. 59 is a view of a retort at the Royal Gunpowder Factory, Waltham Abbey; it is provided with a stirring arrangement, *B*, and man-holes, *A* and *C*, for filling and emptying. The tubes for the gases and vapours have rods, *K*, to remove any obstruction of tar, coke or dust. The charge of such a retort is from 300 to 700 lb. After fastening down the man-hole the stirring mechanism is started and the retort is gradually heated up, care being taken to avoid over-heating as far as possible, as it causes the

[1] For statistics *see J.S.C.I.*, 1914, p. 345.

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formation of tar and coke, and a corresponding diminution of the yield of acetone. It is not practicable to dry the whole of the moisture out of the acetate before charging it into the retort, as acetone begins to be given off even at a moderate temperature. Consequently the first runnings of the retort consist of water with only a little acetone. The decomposition of the acetate does not become active until the temperature reaches about 380° C.; the bulk of the distillate comes over between 380° and 400° C. At the end of the distillation steam is blown through to remove the last portion of the distillate, and to render the residue in the retort uninflammable.

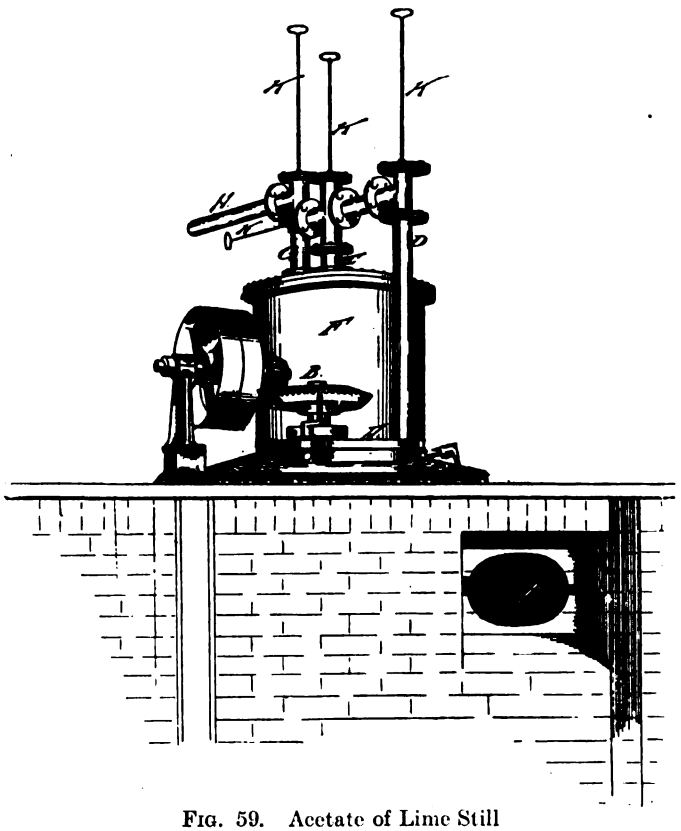

FIG. 59. Acetate of Lime Still

Attempts have been made to heat the retorts in a bath of lead in order to make the heating more uniform and so improve the yield, but trouble was caused by the oxidation of the lead, with the consequence that heat was lost, and the special object of the bath was not attained. Heating in a stream of superheated steam has also been tried: a better yield is thus obtained, but the consumption of fuel by this process is considerably greater; moreover, it is only possible to work sifted, dust-free acetate, which makes it very expensive. Another process, that has been tried and abandoned, was the conversion of the acetic acid of the crude pyroligneous acid directly into acetone without the preliminary formation of acetate. This was done by passing the acid over heated baryta or lime. A plant was erected on this principle in Woolwich Arsenal, but it did not prove successful, and was soon abandoned. The yields by this process were very poor; the crude acetone was mixed with much unchanged acetic acid, which had to be recovered and worked over again.

Recently an improvement has been effected by heating the acetate in thin layers, that are not in direct contact with the hot walls of the retort. Fig. 60

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shows a retort on this principle made by F. H. Meyer, of Hanover. The trays of acetate are placed on trolleys, two of which are wheeled bodily into the retort. The latter is heated as uniformly as possible by means of a number of fires. When the charge is finished, the trolleys are wheeled out and two fresh ones are run in at once. Thus loss of heat is avoided, and the disagreeable operation of drawing the very dusty spent lime from the retort is much improved.

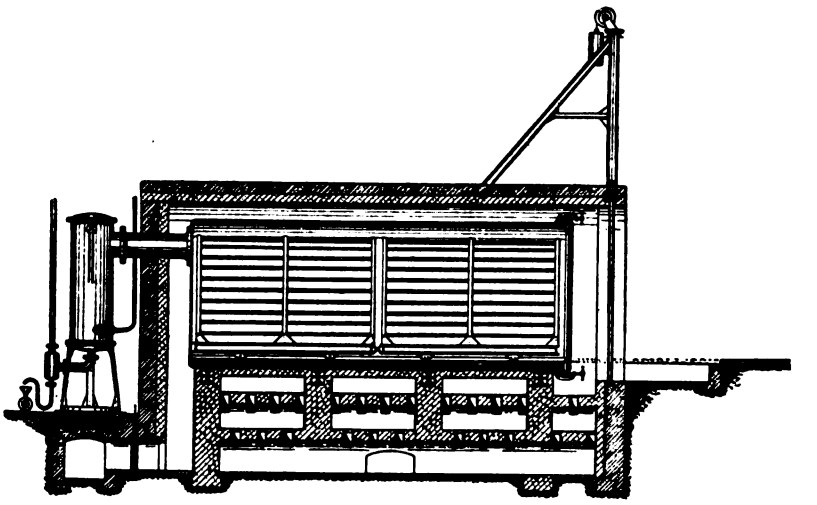

FIG. 60. F. H. Meyer's Plant for the Dry Distillation of Acetate of Lime

From the retort the vapours are led to a condenser, which must be so constructed that the tubes can easily be cleaned, as they are liable to become choked with tar and dust. The crude distillate separates into two layers, the heavier of which consists mostly of water and acetone with some methyl-ethyl-ketone and other impurities, the lighter one of methyl-ethyl-ketone and tarry matter with impurities such as dumasin, and there is some water and acetone dissolved in it. The mixture is pumped into a tank rendered alkaline with caustic soda and allowed to settle. The heavier layer is then run off, and the lighter is washed several times with water. These collected liquors are then pumped into a still, such as that shown diagrammatically in Fig. 61. The essential feature of this is that part of the vapour is condensed in the tubular condenser, *D*, and returned to the column, *C*, where it flows over a number of perforated plates. The passage of the vapour through each of these plates is equivalent to a fresh fractionation. The remainder of the vapour passes down the tube, *F*, to the condenser, *D*. From this the liquid flows through the still-watcher, *H*, to a drum or other receiver.

With such a distilling plant there is no difficulty in getting the acetone free from water, but the removal of the other impurities causes considerable trouble. As the distillate runs through the still-watcher, continuous observations of the specific gravity are taken by means of a hydrometer floating in the liquid: all that shows a higher gravity than ·800 is run into a separate receptacle for impure acetone, but it is afterwards redistilled to recover the good acetone.

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Permanganate test. One of the principal tests applied to acetone is the " permanganate test " : according to the specification of the English Government 1 c.c. of a 0·1 per cent. solution of potassium permanganate is added to 100 c.c. of acetone, and the characteristic colour of the permanganate must persist for at least half an hour. Only the middle portion of the distillate will stand this test. The soda added to the crude acetone combines with all free acid, so that the distilled acetone contains no acid except a little carbon dioxide. The greater part of the aldehyde is also removed by the soda, as it converts it into resinous bodies, which are not volatile, and consequently remain in the still ; the distillate only contains traces of aldehyde.

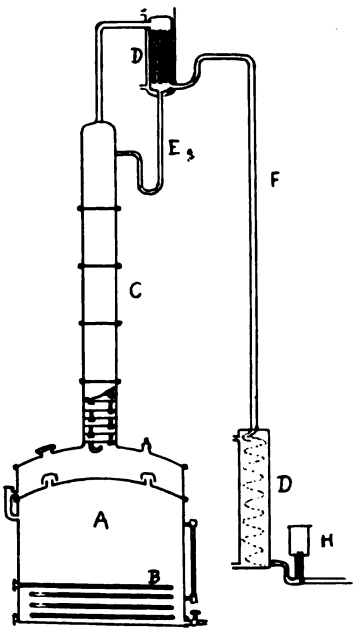

FIG. 61. Still for Rectifying Acetone or Alcohol

Impurities. There are other impurities, however, which pass over and greatly affect the permanganate test. Moreover, it is found that acetones, which pass the test with ease when quite fresh, fail after having been kept some time. The fall of the test is often very rapid at first, but becomes slower after a time, but even after years the fall may still continue. The fall of the permanganate test is generally accompanied by an alteration in the colour of the acetone, which assumes a brown colour instead of remaining colourless. Such deteriorated acetone is considered unfit for the manufacture of cordite and similar explosives, and has to be redistilled before use. As the English Government maintains a large reserve of acetone, amounting to several years' consumption, this redistillation became a serious matter not only on account of the actual cost of the redistillation, but also because there was a considerable loss of acetone during distillation, and in the first and last runnings. The cause of the deterioration was therefore investigated and was found to be intimately associated with the presence of basic substances such as methylamine in the acetone. If after the first distillation in the presence of soda the acetone is distilled again, but this time with the addition of a small excess of sulphuric acid to the liquid in the still, all basic substances are entirely removed ; the redistilled acetone gives a much better permanganate test, which, moreover, falls off little or not at all even after storage for several years.[1]

Amines. Of the various amines that may be present in acetone, the primary and secondary amines are those that have the most deleterious effect on the keeping

[1] *See* Marshall, *J.S.C.I.*, 1904, p. 645.

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powers of acetone, *e.g.* methyl-amine, ethyl-amine, butyl-amine, amyl-amine; dimethyl-amine, diethyl-amine. On the other hand, ammonia and tertiary amines such as trimethyl-amine have little or no effect upon it. The principal amine present in acetone that has not been distilled over acid, is mono-methyl-amine together with some ammonia, and the amount is usually between 0·0005 and 0·005 per cent. Although these quantities are small, they are sufficient in the presence of quantities of aldehyde of the same order to cause a decided deterioration of the acetone. Ammonia and the primary amines form more or less stable compounds with acetone, which are only gradually decomposed again during distillation, with the result that the amine comes over in varying quantities in all parts of the distillate instead of only in the first runnings. It is not the formation of these compounds, however, that causes the deterioration of the acetone, but the action of the amines on the traces of aldehyde and other impurities, or perhaps simultaneous action on these substances and acetone.

Aldehydes.

The acetate of lime contains a considerable proportion of calcium formate, and this in the dry distillation gives rise to aldehydes. Acetaldehyde is probably the principal one, but there are also formaldehyde, propionic aldehyde, and other higher members of the series. Formaldehyde readily changes into a mixture of methyl-alcohol and formic acid during the dry distillation, and also during the distillation with soda. The formic acid, of course, remains in the still as sodium formate, but the methyl-alcohol passes over into the distillate, and is found especially in the first runnings. Acetaldehyde, when acted upon by the alkali, is largely converted into aldol and other high-boiling condensation products and into resinous bodies, which remain in the still. Propionic and other aldehydes behave very much in the same way as acetaldehyde. The destruction of the aldehydes is not complete, however, and consequently small traces are to be found in the acetone even after several distillations.

The presence of small traces of aldehyde can be detected in acetone by the application of Schiff's reagent. Acetone itself gives a purple coloration, but if there be 0·005 per cent. of acetaldehyde or methylal in it, the colour is distinctly stronger.

Methyl-alcohol.

Methyl-alcohol, as has already been pointed out, is produced from the formaldehyde. There are many other reactions by which it can be formed from the constituents of crude pyroligneous acid. As methyl-alcohol has a boiling-point, 65·5°, considerably higher than that of acetone, 56·1°, and has practically the same specific gravity, 0·796, it might be thought that the alcohol would pass over in the last runnings of the distillation, and that its presence would not affect the specific gravity of the acetone. The reverse is, however, the case. When the two liquids are mixed together, there is a contraction, and consequently the mixture is more dense than the con-

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stituents. Moreover, mixtures containing much acetone boil at a lower temperature than acetone itself; the mixture of minimum boiling-point contains 86·5 per cent. of acetone, and 13·5 per cent. of methyl-alcohol, and boils at 55·9°.[1] This mixture has a specific gravity of 0·7997; it cannot be separated into its constituents by fractional distillation; on the contrary it behaves much as a simple liquid. Moreover, as its boiling-point is so near to that of acetone the constant boiling mixture cannot be entirely separated from the acetone. Consequently methyl-alcohol occurs mostly in the first runnings, but is also present throughout the distillation. It is possible that methyl-alcohol may have a deleterious effect upon the stability of explosives with which it is mixed, through its liability to become oxidized to formaldehyde, but as there is no method known for the ready determination of the amount of it in acetone, nor any process for separating it on a manufacturing scale without greatly increasing the cost of the solvent, no particular attention has hitherto been paid to the matter.

Hydro-carbons, etc.

Besides these impurities the first runnings also contain some substances that are insoluble in water: if this acetone be mixed with twice its bulk of water these separate out partly. The liquid thus obtained is a complex mixture with a specific gravity of about 0·78 and boiling over a range of 50° to 110°, it apparently contains various hydro-carbons saturated and unsaturated, and also substances such as furfuran C_4H_4O and sylvan C_5H_6O. Furfuran would be formed by the dry distillation of the calcium salt of pyromucic acid, one of the constituents of the crude pyroligneous acid.

The effect of these substances upon the permanganate test is very similar to that of aldehyde, but not nearly so great. The addition of 0·2 per cent. reduces the permanganate test of pure acetone from many hours to about 100 minutes, and in the presence of basic substances there is a further slow fall, which, however, is not nearly so rapid as in the case of aldehydes. If 0·2 per cent. be present the acetone becomes cloudy on the addition of two volumes of water. Those impurities can be separated by a special process of distillation, for which *see* Part XI. There are also chemical reactions by which these substances can be detected and estimated: such as the iodine test given in Part XI, which enables one to estimate the amount of the substances to within 0·002 per cent. Commercial acetones usually contain from 0·02 per cent. to 0·10 per cent., average 0·04 per cent. There appears to be no reason to think that these small quantities can have any appreciable effect on the stability of explosives, either beneficial or otherwise.

The presence of these substances insoluble in water is not confined to the first runnings: there is almost as much of them in the last runnings and, even the middle fractions contain usually 0·02 to 0·04 per cent., as may be ascertained by the application of the tests just mentioned.

[1] Pettit, *Jour. Phys. Chem.*, 1899, 3, 349.

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When the main bulk of the acetone has distilled over, the temperature of the still-head and the specific gravity of the distillate commence to rise: after a short time the temperature reaches about 73·5° and the specific gravity 0·840, and there they remain steady for some time. The distillate now consists almost entirely of a mixture of water and methyl-ethyl-ketone, the next homologue to acetone, in the proportion of 11·4 of water to 88·6 of ketone. This mixture distils unchanged, and the water can only be separated from it by treatment with a dehydrating agent such as calcium chloride or solid caustic soda. In the intermediate fractions, when the boiling-point and the gravity are rapidly altering, the distillate contains much impurity, substances insoluble in water and perhaps ethyl-alcohol. Afterwards, when the boiling-point becomes constant, the constant boiling mixture comes over in a state of considerable purity. Then after a time the boiling-point rises again, and a distillate is obtained which still separates out into two layers, the lighter of which consists mostly of higher ketones with a small proportion of water and impurities, and the lower largely of water.

Methyl-ethyl-ketone, when freed from water, gelatinizes gun-cotton as well as acetone, and has no bad effect upon it. It would be possible to add a considerable proportion of it to acetone without causing it to fail in any of the usual specification tests, but it is more usual to sell it separately for denaturing spirit and dissolving resins. The heavier acetone oils are also used for making lacquers, etc., but do not command a very good price.

Acetone from starch.

It has been discovered by Fernbach that starch can be submitted to a process of fermentation whereby it is converted into a mixture of fusel oil and acetone, and it has been proposed to convert the fusel oil into artificial rubber, whilst the by-product acetone can be purified and placed on the market.[1] It remains to be seen whether these processes can be developed so as to be remunerative. It has been stated that from 100 parts of dry potato substance a yield of 22 parts of rubber and 14 of acetone can be obtained.

Recovery of solvents.

As but little of the solvent is allowed to remain in the finished powder, it is advisable to recover as much as possible in order that it may be used again. A considerable proportion is lost during the operations of forming the dough into cords, strips, tubes or flakes, and hitherto there has been little attempt to recover this portion, as the difficulties introduced into the carrying out of the operations would absorb too much of the profit on the recovery. It is only from the drying stoves that recovery is attempted as a rule. When the solvent is ether-alcohol difficulties are introduced by the great volatility of the ether: by drawing the air away from the stoves through cooling coils only alcohol is recovered generally. A greater bulk of condensate can be obtained by using refrigerated water or brine, but if the temperature of the

[1] *See* Perkin, *J.S.C.I.*, 1912, p. 616; also *C.T.J.*, June 29, 1912.

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coils be reduced much below 0° C. there is danger of the coils being choked with ice. In the manufacture of artificial silk by Chardonnet's process attempts have been made to recover the solvent by passing the air up towers, where it is scrubbed with a mixture of sulphuric acid and water or with oil. T. Chandelon proposes to use the chlorine, eramine or nitro-derivatives of aliphatic or aromatic hydrocarbons for the recovery of ether and alcohol from air.[1] It has also been proposed to compress, cool and re-expand the air in a regenerative machine as is done in Linde's plant for the manufacture of liquid air, but whether recovery of the solvent by such a process would prove remunerative seems doubtful.[2]

At the French Government works at Saint-Medard the solvent is recovered from Poudre B by the following method: A trolley charged with strips of powder is run over a metal chamber; a door opens in the top of the chamber just large enough for the trolley to pass through; it is let down and the door is closed, and the vapours of alcohol and ether are given off in the air-tight chamber. They are drawn off by a steady current of air, condensed by refrigeration and collected. When the drying is sufficient the trolley is removed. It is stated that the recovery is satisfactory.[3]

A higher yield of recovered solvent can be attained, if the air after passing through the condenser is returned to the stove, so that it passes constantly round a closed circuit. The evolution of solvent is rapid at first, but becomes slower and slower as the powder gets dryer: large-sized powders for heavy ordnance may have to remain in the stove for months, during the greater part of which time the quantity of solvent vapour given off is hardly appreciable. In laying out works it is advisable to place a few stoves fitted with recovery plant near the press-houses, so that the powder can be transferred to them expeditiously, and dried there for a few days. After this preliminary drying the powder can be transferred to other stoves situated at a distance, where no attempt is made to recover the solvent. Where considerable quantities of powder of large size are made, the area covered with stoves may extend over many acres, and to connect them all up with a recovery plant would be very costly.

Acetone recovery.

For the recovery of acetone from cordite and other materials Robertson and Rintoul have taken advantage of the fact that the vapour is very readily absorbed by a solution of sodium bisulphite, with which it forms a compound, C_3H_6O, $NaHSO_3$.[4] A very simple and satisfactory method has been worked out, by which practically the whole of the acetone in the air of the stove is recovered in a very pure condition. The air is drawn away from the stove through wide galvanized iron pipes to the recovery house where it is caused

[1] Germ. Pat. 254.913 of February 22, 1912.
[2] *See* Worden, pp. 492–496.
[3] *P. et S.*, 16, 1912, p. 108.
[4] Eng. Pat. 25,994 of 1901; U.S. Pat. 723,311 of 1903.

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to pass up a series of towers, down which a 30 per cent. solution of the bisulphite is flowing. Towers were designed specially for this purpose,[1] and they have

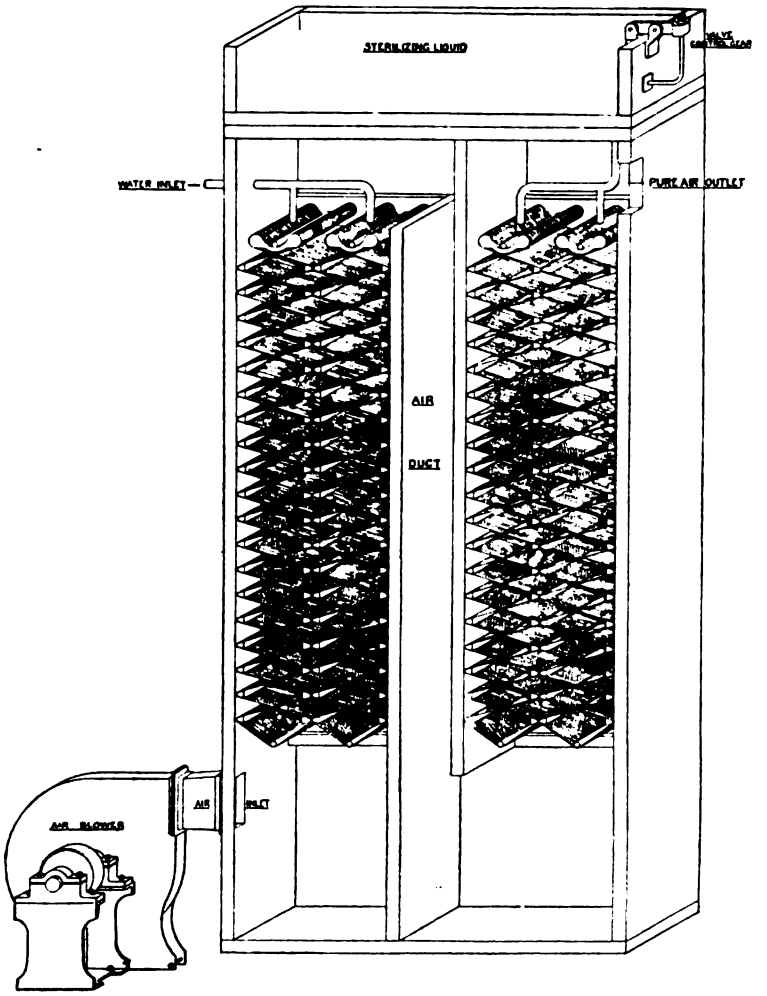

FIG. 62. Scrubbing Towers (Robertson and Rintoul's Patent)

proved very successful not only for this, but for many other purposes also such as purifying air (*see* Fig. 62), as they afford a maximum surface of contact between the air and the liquid, and offer a minimum of resistance to the passage of the former. The towers are square in section and lined with lead : inside there are frames, which are wound with strands of wool zig-zag fashion. At

[1] Eng. Pat. 25,993 of 1901.

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the top of the tower each strand dips into a trough, which is kept supplied with bisulphite solution. The top of the tower is closed by means of a glass plate, and there is also a glass window near the bottom, so the action of the tower can be watched. There are, of course, various pumps or eggs and tanks, so that the solution can be raised again and passed down the same tower again, or the next one nearer the stove. When the solution is nearly saturated with acetone it is transferred to a still, where it is simply heated to drive the acetone off again, as it has been found that practically the whole of the acetone can be distilled off before the bisulphite begins to decompose. A little sodium carbonate is added, however, to diminish the amount of sulphur dioxide that passes over, and to combine with any free sulphurous acid that has been formed by the oxidation of the bisulphite, and the consequent formation of sodium sulphate. The crude distillate thus obtained is mixed with water and a little sodium carbonate, and distilled again from a still such as that shown in Fig. 61. It is thus obtained in an extremely pure state; it contains no detectable quantity of any impurity except some ethyl-methyl-ketone, which is harmless, and a trace of carbonic acid. The bisulphite solution is prepared by passing sulphur dioxide into a solution of sodium carbonate, the sulphur dioxide being made by burning sulphur in a small burner in a current of air.

Volatility of the nitro-glycerine.

Another reason for not attempting to recover the acetone from the last stages of the drying of a nitro-glycerine powder is that nitro-glycerine is given off much more readily when the greater part of the acetone has been removed. Fig. 63 shows how rapidly the vapour tension of the nitro-glycerine rises when the percentage of acetone is very small.[1] In the case of cordite the problem is complicated by the presence of gun-cotton, and the vapour pressures of mixtures of gun-cotton and acetone have not been determined. It is probable, however, that in the freshly pressed cords, containing a fairly large percentage of acetone, a considerable proportion of it is dissolved in the nitro-glycerine, thus reducing the vapour pressure of the latter, but when the percentage of acetone has been reduced to a small amount by drying, nearly the whole of it is dissolved in the gun-cotton, so that the nitro-glycerine exerts nearly its full vapour pressure. The result of this is, that in the early stages of the drying there is little or no danger of nitro-glycerine being deposited in the pipes leading from the stove to the recovery house, but in the later stages it will be deposited. Care must be taken therefore in laying the pipes that the nitro-glycerine will only accumulate in places from which it can be drawn off. At all the lowest points of the pipe-run small draining tubes must be provided; these can be closed with rubber corks, so that the nitro-glycerine can be drawn off daily into a rubber or gutta-percha bottle or beaker.

Another danger that has to be guarded against is the communication of

[1] Marshall, *J.C.S.*, T. 1906, 89, p. 1350; *Proc.* 1913, p. 157.

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fire from one stove to another through the pipe-lines. In Robertson and Rintoul's system protection is afforded by the introduction of traps, in which

Vapour explosions.

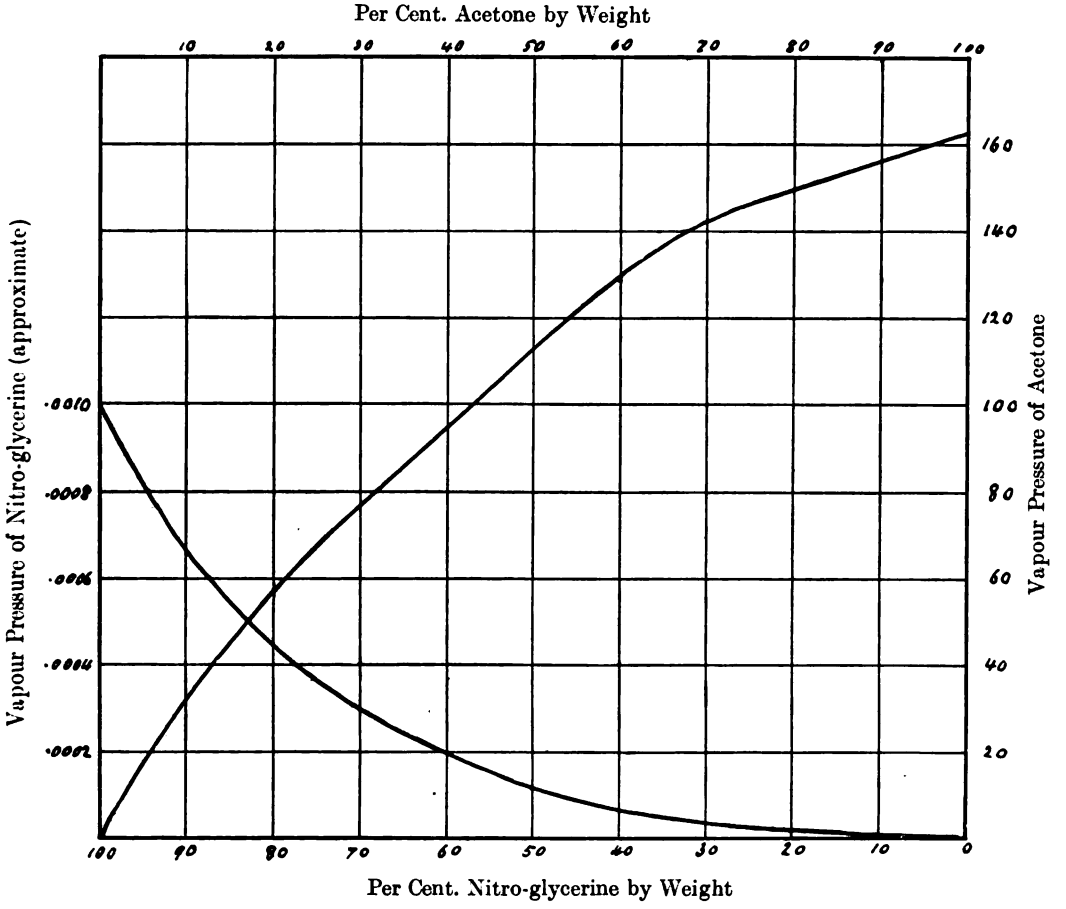

FIG. 63. Vapour Pressures of Mixtures of Acetone and Nitro-glycerine

fine wire gauze is interposed to prevent the further travel of the flame. They are so arranged that a gas explosion in the pipe will blow out a disc of thin material and so relieve the pressure.

It is not only in the pipe-lines that the explosibility of mixtures of vapour and air has to be guarded against, but wherever combustible and volatile liquids are used; in the incorporating and press houses, stoves, magazines and solvent store-houses, great care must be taken that no flame or spark may ignite a mixture of air and vapour. The following Table

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gives the explosive limits for a number of volatile liquids as determined by Kubierschky : [1]

	Percentages by Volume		Per cent. by Weight corresponding to 1 per cent. by Vol.
	Lower Limit	Upper Limit	
Benzene	1·4	4·7	2·77
Toluene	1·4	—	3·20
Ethyl-alcohol	4·0	13·6	1·61
Methyl-alcohol	7·8	(18·0)	1·12
Acetone	2·7	—	2·02
Ether	1·8	5·2	2·56
Carbon bisulphide	4·1	—	2·64
Benzine	2·6	(4·8)	—
Pentane	2·5	(4·8)	2·51

If the percentage of vapour fall below the lower limit or rise above the upper, the mixture is no longer inflammable, but these limits depend upon the conditions under which the experiment is carried out. In a large flask the limits are wider than in a narrow tube, and a small spark often will not ignite a mixture that can be caused to explode by the application of a powerful spark or a flame.[2] The limits are much narrowed by the introduction of carbon dioxide or other indifferent gas. It has been shown by Olié [3] that the introduction of a jet of steam will extinguish a large quantity of fiercely burning alcohol in a few minutes, and it is recommended that buildings containing considerable quantities of inflammable liquids be fitted up so that a fire can be extinguished by this means. It must not be forgotten that vapours may be ignited by electric sparks generated by the friction of driving belts, and precautions should be taken to dissipate any charges that may be thus formed.

Even the empty drums which have contained liquids may give rise to serious accidents if the last traces are not removed. On March 30, 1904, a drum, that had contained acetone exploded, killing two men and injuring several others at Prince's Dock, Glasgow. The drums when emptied should be left without their bungs and should be placed upon racks in the open for a few days with the bungholes downwards : if at the end of that time it is found that the smell of the solvent is still perceptible in the drum, the last traces can be removed by directing a jet of compressed air into the drum for a minute or so, relying on the absence of smell as an indication that the removal

[1] *Ang.*, 1901, p. 130.
[2] *See also* Bunte, *J. f. Gasb.*, 1901, p. 1835 ; *J.S.C.I.*, 1902, p. 33.
[3] *P. et S.*, 15, 1910, p. 160.

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is complete. The bungs should then be replaced and screwed up so tightly by means of a key that it is impossible to remove them by hand, or for them to work loose during transit.[1]

The vapours of many of the liquids used as solvents are injurious to the health of those exposed to them. Benzene is very poisonous, but is not used much for making smokeless powders. Acetone has no very serious effect. That of the alcohols increases with the molecular weight; amyl-alcohol is decidedly the worst of those generally used. It has been found that the following doses are fatal per kg. of animal :[2] **Toxicity of vapours.**

Methyl-alcohol	. . . . .	6·00 g. per kg.	
Ethyl ,,	(absolute)	7·75 ,,	,,
Propyl ,,	. . . . .	3·75 ,,	,,
Butyl ,,	. . . . .	1·85 ,,	,,
Amyl ,,	. . . . .	1·50 ,,	,,

A mixture of the vapours of ether and alcohol is more poisonous than that of either of the substances separately. For this reason also buildings in which amyl-alcohol or ether-alcohol vapours may be present should be well ventilated.

[1] *A. R.*, 1904, p. 94.

[2] *P. et S.*, vol. xvi., 1912, p. 128.

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PART VII

BLASTING EXPLOSIVES

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CHAPTER XXII

NITRO-GLYCERINE HIGH EXPLOSIVES

Kieselguhr : Manufacture of dynamite : Properties of dynamite : French dynamites : American dynamite : Ligdyn : Ammonia dynamite : Judson powder : Dynamite Nos. 2 and 3 : Gelatinized explosives : Boxes for jelly : Diminution of sensitiveness and stability : Gelignite : Gelatine dynamite : Wrappers : 40 per cent. dynamite : American gelatin dynamites : Forcite : French gelatinized explosives : Low freezing explosives : Safety explosives containing nitro-glycerine : Carbonites

Kieselguhr.

THE first attempts to use liquid nitro-glycerine for blasting proved so disastrous, that it became necessary to find some means of converting it into a solid, unless its wonderful power was to be lost to the world. Many of the principal countries had indeed passed laws forbidding the use of nitro-glycerine, when in 1866 Nobel discovered that it could be rendered comparatively safe by absorbing it in kieselguhr. This at once gave a great impetus to the high explosives industry and laid the foundations of the great fortune, which Nobel afterwards increased by other inventions and by his financial ability. Kieselguhr or guhr is a fine siliceous earth consisting of the remains of diatoms and other microscopic animals. It should have the power of absorbing three times its weight of nitro-glycerine, and should be free from gritty particles. It is found in the Lünerburger Heide, to the north of Hanover, also in Austria, Scotland, Norway, and Australia. The following analyses show its composition :

	From Oberlohe (Hanover)		Dried	Calcined
	Top Stratum	Second Stratum		
	(Gody)	(Gody)	(Sanford)	(Hagen)
Silica	87·85	74·48	94·3	96·34
Calcium carbonate	·73	·34	—	—
Lime	—	—	—	1·64
Magnesia	—	—	2·1	—
Iron oxide	·73	·39	1·3	·5
Alumina	·13	—	—	1·5
Organic matter	2·28	24·42	·4	—
Moisture	8·43		1·9	

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A sample of the guhr used at Ardeer in 1884 was analysed by Dupré (*S.R.* 61): it was of pale red colour and passed entirely through a 20-mesh sieve; it consisted of:

Soluble silica, oxide of iron	95·69
Insoluble silica, sand and grit	2·00
Loss on ignition	0·60
Moisture	1·71
	100·00

Guhr is decidedly hygroscopic and cannot be dried effectively except at a high temperature: it is necessary to calcine it at a low red heat. The organic matter is thus destroyed also. Sometimes, however, the guhr is only charred, in which case a considerable percentage of carbonaceous matter will remain. The guhr may be mixed with some ochre, mica, talc or barium sulphate without impairing its absorptive powers. Ochre gives the dynamite a uniform red colour. Carbonate of ammonium, sodium, magnesium or calcium is added up to 2 per cent. of the finished explosive, in order to neutralize the acid formed by the decomposition of the nitro-glycerine on storage. The carbonates of magnesium and calcium are best, as the others have a decomposing action on the explosive.

Manufacture of Dynamite.

The carbonate and other additions should be mixed very intimately with the guhr, which is then passed through a 30-mesh sieve to remove all foreign bodies. The material is then weighed out into a lead, brass or copper-lined box, or a rubber bag, and nitro-glycerine is poured on in the proportion of not more than 75 parts by weight to 25 of the absorbent. After standing for a time the material is kneaded or mixed by hand in much the same way as is done with cordite paste. The mixture is then conveyed to a cartridge hut in which are erected two to four, but preferably only two, cartridge machines. Each of these consists of a brass plunger working vertically through two sleeves or guides (Fig. 64). It is worked by means of a hand-lever, and is shod at the lower end with lignum vitæ or ivory. This lower end works in a thin brass tube of the same diameter as the finished cartridge is to be. The upper end of the tube forms the apex of an inverted cone or hopper of soft leather (not shown in the illustration), having a capacity of about a pound of dynamite, the upper edges of this hopper being connected by three or more cords to a boss higher up on the plunger. The plunger works easily through the guides, so as to minimize the friction, and there is a good clearance between it and the tube. Sometimes it carries an inverted bell to prevent the explosive working up into the lower guide. To work the apparatus a girl wraps a paper cartridge wrapper round the outside of the tube, leaving sufficient paper at the bottom to turn in and close the end. Holding this in position with one hand she works the pump handle with the other; the effect of each upward stroke is to jerk the

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soft leather hopper by means of the cords, and cause the contained dynamite to fall into the tube, whence it is forced by the ensuing downward stroke into the paper wrapper at the lower end of this tube; this is repeated until the cartridge is of the required length, when it is removed, and the upper end of the paper is folded in.

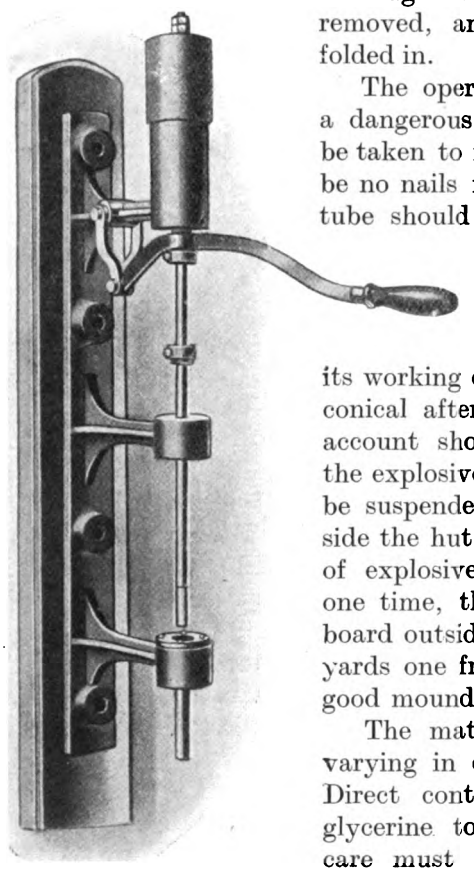

FIG. 64. Dynamite Cartridge Machine

The operation of making these cartridges is a dangerous one, and the greatest care should be taken to minimize the danger.[1] There should be no nails in the machine; the mouth of the tube should be bevelled and faced with leather so fitted that an untrue plunger cannot strike the edge of the tube; the diameter of the body of the plunger should be less than that of its working end; and the tube should be slightly conical after the first short distance. On no account should any attempt be made to work the explosive when it is frozen, and work should be suspended altogether if the temperature inside the hut is below 50°. Only a small quantity of explosive should be allowed in the hut at one time, the remainder being kept in a cupboard outside. The huts should be at least 40 yards one from another, and surrounded with good mounds.

Properties of Dynamite.

The material thus made is a plastic mass varying in colour from buff to reddish brown. Direct contact with water causes the nitro-glycerine to separate from it; therefore great care must be exercised when using it in wet places. It freezes somewhat more readily than liquid nitro-glycerine. When ignited in small quantities it simply burns away fiercely, but fatal accidents have arisen in considerable number from persons supposing that, as it is reasonably safe to ignite a few cartridges of unfrozen dynamite, it is equally safe to warm it upon a shovel, in an oven, in a tin over a fire, or in various other ways, which usually lead to a verdict of "Accidental Death." Frozen dynamite is much more susceptible to explosion by simple ignition, but it is less sensitive to detonation, as also to a blow or friction under some conditions, but the annals of explosives are full of instances of the fatal

[1] *See S.R.*, 61, Nos. 145 and 184.

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unexpected explosion of frozen nitro-glycerine explosives, which had not been treated with proper respect.

The following are analyses made by Dupré in 1901 of two samples from Ardeer :

Nitro-glycerine	73·62	..	73·98
Kieselguhr	25·70	..	25·00
Ammonium carbonate	0·19	..	0·16
Other soluble matter	0·11	..	0·24
Moisture	0·38	..	0·62
	100·00	..	100·00
*Containing sand, calculated on dynamite	0·1	..	0·15
,, ,, ,, Kieselguhr	0·39	..	0·61

Both samples were of a light brick red colour and gave heat tests of over thirty minutes.

This material is called in Great Britain Dynamite No. 1, or Kieselguhr Dynamite, or simply Dynamite, and in Germany the nomenclature is much the same, but in America it is called Giant Powder, and the term dynamite is usually applied to a mixture of nitro-glycerine, wood pulp and sodium nitrate, which is not authorized in England at all. Dynamite No. 1 is not made very extensively now, as it has been replaced by various gelatinized nitro-glycerine mixtures, but it possesses the advantage that it is more stable when stored at high temperatures, as the acid products of decomposition are immediately neutralized by the carbonate present. I have examined dynamite that had been stored for a considerable number of years at Aden, and could find no signs of instability, whereas a gelatinized explosive under the same conditions would have given a very low heat test.

Besides infusorial earth other siliceous materials have been used for the manufacture of dynamite ; in France, for instance, a material called Randanite, which is found in Auvergne, and has been formed by the weathering of feldspar. Berthelot proposed the use of a special artificial silica made by decomposing silicon fluoride with water and having a very high absorptive power. Nobel, in his patent specifications, mentioned a number of materials such as powdered brick, dry clay and plaster. During the siege of Paris coal-ashes were used, and in America magnesium carbonate has found some favour. The following are the compositions of dynamites made at Vonges, in France :

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French dynamites	No. 1	No. 2	No. 3	Special
Nitro-glycerine	75	50	30	90
Randanite	20·8	—	—	1
Vierson silica	3·8	48	—	—
Launois silica	—	—	60	—
Special silica	—	—	—	8
Magnesium carbonate	0·4	—	—	1
Meudon chalk	—	1·5	—	—
Carbonate of lime	—	—	1	—
Blast furnace slag	—	—	4	—
Red ochre	—	0·5	—	—
Yellow ochre	—	—	5	—

As nitro-glycerine contains an excess of oxygen even after all the carbon has been converted into dioxide, the idea naturally occurred to mix it with an organic absorbent: cork charcoal has a very great absorptive power, but the material that has been used most is wood pulp. The "Atlas Powders" introduced from America by the Fenians in 1883 and 1884 for their criminal attempts were of this type. Two of the samples analysed by Dupré had the following composition:

American dynamites.

Nitro-glycerine	29·8	Nitro-glycerine	71·6
Wood sawdust slightly charred in parts	63·8	Wood sawdust and a little chalk	24·9
Moisture	6·4	Moisture	3·5

But these mixtures contained an excess of oxidizable matter. It is more economical to add another oxygen carrier. In America sodium nitrate is used very extensively for this purpose. In the Bureau of Explosives Report No. 2, Beistle gives the results of the analysis of a large number of American dynamites, which are summarized in the following Table:

Grade	Nitro-glycerine	Wood Pulp	Sodium Nitrate	Moisture
60 per cent.	53·5–65·1	14·2–21·0	16·0–29·8	1·16–3·18
50 .,	49·3–50·1	11·6–13·4	32·6–33·8	1·97–2·00
40 .,	34·8–41·9	7·7–13·9	38·4–50·2	0·80–3·60
30 .,	29·7–32·5	7·9–10·2	52·6–60·1	1·09–1·69

It will be seen that the variations in composition in each grade are considerable; the figures for the 50 and 30 per cent. grades are based on two analyses each only, but those for the other grades on a considerable number. Many of the

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dynamites evidently contained a few per cent. of some other constituents undetermined, but those in which there was a considerable deficit have been excluded from the above summary The following are two examples of American 40 per cent. dynamites:

	Straight dynamite	Hercules
Nitro-glycerine	40	40
Wood-pulp	11·75	11
Sodium nitrate	47·25	45
Calcium carbonate	1	—
Magnesium carbonate	—	1
Sodium chloride	—	1
Moisture	—	2

Hall and Howell give the following as the composition of typical American "straight" dynamites: [1]

Ingredients	15 per cent.	20 per cent.	25 per cent.	30 per cent.	35 per cent.	40 per cent.	45 per cent.	50 per cent.	55 per cent.	60 per cent.
Nitro-glycerine	15	20	25	30	35	40	45	50	55	60
Combustible material [2]	20	19	18	17	16	15	14	14	15	16
Sodium nitrate	64	60	56	52	48	44	40	35	29	23
Calcium or magnesium carbonate	1	1	1	1	1	1	1	1	1	1
	100	100	100	100	100	100	100	100	100	100

Ligdyn.

A similar explosive is manufactured in South Africa under the name of Ligdyn. The 40 per cent. grade has the composition:

Nitro-glycerine	40
Wood-meal	13
Sodium nitrate	45
Wheat flour	2

The cartridges are made in the Quinan packing machine, which works on the same principle as the hand machine shown in Fig. 64, but it is operated by power, and makes thirteen to fifteen cartridges at one time. On January 3, 1913, the contents of one of these machines exploded and killed nine persons and injured two others.

Ammonia dynamites.

In America Ammonia Dynamites are also made, in which a large proportion of the nitro-glycerine is replaced by ammonium nitrate.

[1] Bureau of Mines Bulletin, No. 48.

[2] Consisting of wood-pulp, flour, and sulphur for grades below 40 per cent.; wood-pulp only for other grades.

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The following Table shows the compositions of typical ammonia dynamites of various grades [1]:

	30 per cent.	35 per cent.	40 per cent.	50 per cent.	60 per cent.
Nitro-glycerine	15	20	22	27	35
Ammonium nitrate	15	15	20	25	30
Sodium nitrate	51	48	42	36	24
Combustible material [2]	18	16	15	11	10
Calcium carbonate or zinc oxide	1	1	1	1	1

Judson powder.

An explosive of a somewhat different type, which is also used extensively in America, is Judson Powder. This is made with percentages of nitro-glycerine varying from 5 to 20 per cent. Judson Powder R.R.P. has the composition:

Nitro-glycerine	5
Sodium nitrate	64
Sulphur	16
Cannel coal	15

It is really a sort of crude gunpowder containing a little nitro-glycerine. It is fired with a priming cartridge of dynamite.

The great objection to these mixtures is that sodium nitrate is decidedly deliquescent, and ammonium nitrate still more so: even from a moderately dry atmosphere they take up moisture and become liquid, and the solution thus formed displaces the nitro-glycerine and causes it to exude, thus giving rise to a very serious danger. For this reason such explosives have never been authorized in England. It is noteworthy that for the work on the Panama Canal, in which many millions of tons of dynamite have been used, the Isthmian Canal Commission only accepted explosives containing potassium nitrate and free from sodium nitrate, magnesium salts and other impurities which would make the material hygroscopic. Two samples of Atlas Powder used in the construction of the Panama Canal were analysed by Stillman and had the composition:

	B +	C +
Nitro-glycerine	61·1	45·7
Wood-pulp	14·1	10·5
Potassium nitrate	21·6	40·9
Magnesium oxide	3·0	—
Chalk	—	1·9
Moisture	0·2	1·0

[1] Hall and Howell, *loc. cit.*

[2] Consisting of wood-pulp, flour, and sulphur.

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Dynamite Nos. 2 and 3.

The early demand for an explosive that was milder and slower than Dynamite No. 1 was met in England by the manufacture of Dynamite No. 2, which was recommended for work in coal-mines and quarries. This consisted of not more than 18 per cent. of nitro-glycerine mixed with some 10 per cent. of charcoal and 72 per cent. of saltpetre, and sometimes a little paraffin. It was practically gunpowder in which nitro-glycerine had been substituted for sulphur. Dynamite No. 3 was a more powerful explosive, and consisted of a mixture of equal parts of kieselguhr dynamite and a mixture of saltpetre and wood-meal.

Gelatinized explosives.

In 1875 Nobel made a further advance of the very first importance by his discovery that by dissolving 7 or 8 per cent. of collodion cotton in nitro-glycerine it is converted into a gelatinous solid. The discovery arose from the fact that Nobel had cut his finger and collodion had been used to cover the wound: whilst the inventor was experimenting with nitro-glycerine some of it got mixed with the collodion. In the following year patents were granted in the principal industrial countries protecting the invention, but it was some years before the difficulties of manufacture had been overcome. In Great Britain the manufacture was licensed in 1878, and in 1880 the manufacture was commenced on a large scale in the Continental factories of the Nobel Syndicate, but considerable difficulty was found in fulfilling the requirements of H.M. Inspectors of Explosives. The first products exuded nitro-glycerine, and manufacture was suspended for some years: afterwards, when this difficulty had been overcome, the blasting gelatines failed to pass the heat test, and it was not until 1887 that the manufacture was in full swing in Great Britain. A great demand for the material sprang up at once in consequence of its enormous power and convenient nature. For blasting hard rock it has proved very serviceable, especially when, as in tunnelling, it is not necessary to get the rock out in large pieces.

Manufacture.

The collodion cotton is thoroughly dried and reduced to a fine state of division. A weighed quantity is placed in a brass-lined box, and the requisite quantity of nitro-glycerine is poured on. The materials are mixed together by hand and allowed to stand for some hours or overnight. The box is then taken to the mixing house, where the material is heated to about 50° C. and gently mixed until solution is complete, which takes about an hour. At first the mixing was done entirely by hand with wooden stirrers, but now the final mixing is generally performed in incorporating machines similar to those used in the manufacture of smokeless powders (*see* Figs. 51, 52). At the Ardeer Factory of Nobel's Explosives Co. and some other works McRoberts's machine is used (Fig. 65). This has a number of narrow stirrer blades mounted on two vertical spindles, which are driven from above. The trough containing the explosive mixture is wheeled in below and raised by means of suitable gearing. There are stops to prevent the bottom of the trough coming in contact with

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the stirrers. The trough has a double wall, through which hot water can be circulated from a tank outside the building maintained at a temperature of 50° C. The actual temperature of the mixture is 40° to 45°. After about an hour the trough is removed and the gelatine is allowed to stand to get cool and become stiffer. It may be made into cartridges in the machine shown in Fig. 64, or the " sausage machine " illustrated in Fig. 66 may be used for this and other gelatinous explosives that are not too stiff. The gelatine is fed in through the hopper, *b*, whilst the handle is turned. The Archimedean screw forces the material forward and out of the nozzle, the diameter of which corresponds with the size of cartridge to be produced. There are grooves inside the body to prevent the material rotating. In all machines used for working these substances it is essential that only bronze or other suitable alloy be used, and all bearings must be so arranged that the nitro-glycerine cannot

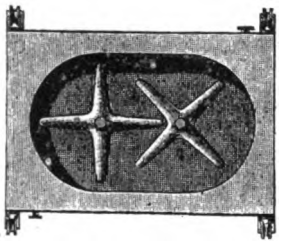

FIG. 65. Plan of McRoberts's Incorporator for Blasting Gelatine

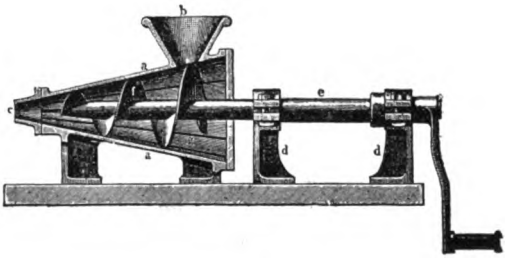

FIG. 66. Cartridge Machine for Gelatinized Explosives

get into them. When the nitro-glycerine is hot it is decidedly more sensitive than when cold.

Boxes for jelly.

The boxes for conveying the mixture of nitro-glycerine and collodion cotton are usually made of wood lined with copper, brass, lead or rubber. There should be no metal on the exterior of the boxes, however, and they should be so constructed as to prevent, as far as possible, those surfaces which are liable to have explosive on them from coming in contact with one another, or with the supports on the bogie, on which they are carried. The boxes should be cleaned thoroughly at frequent intervals. An explosion that occurred at Arklow on August 4, 1911, is ascribed to the neglect of these precautions.[1]

Diminution of sensitiveness

After manufacture blasting gelatine continues to stiffen for a considerable time and, unfortunately, as it gets stiffer it becomes less sensitive to detonation, so that old blasting gelatine may give a missfire. Thus Soddy found that gelatines which gave results of 570 to 600 c.c. in the lead block when first tested, after keeping for a year gave only 340 to 420 c.c. when fired with a

[1] *S.R.*, No. 201.

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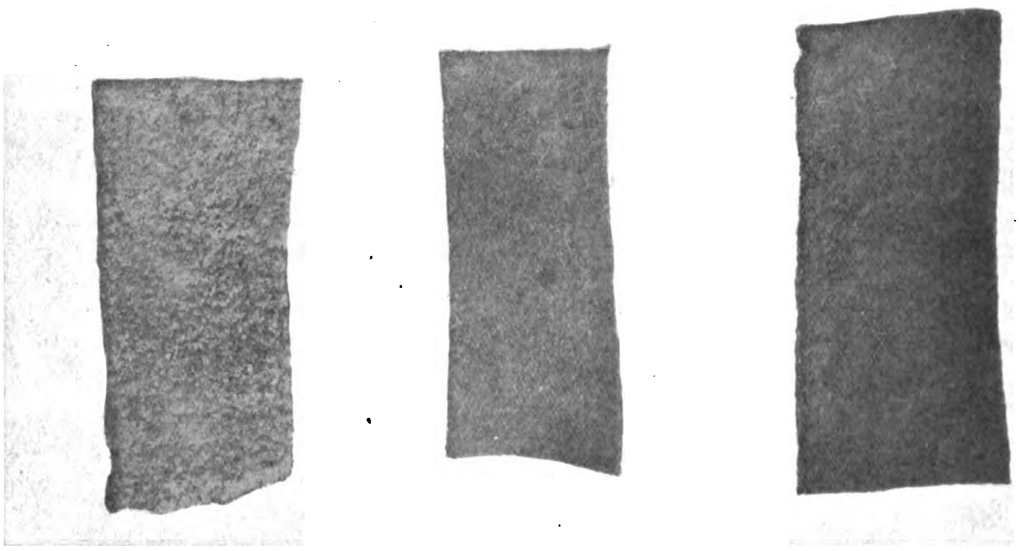
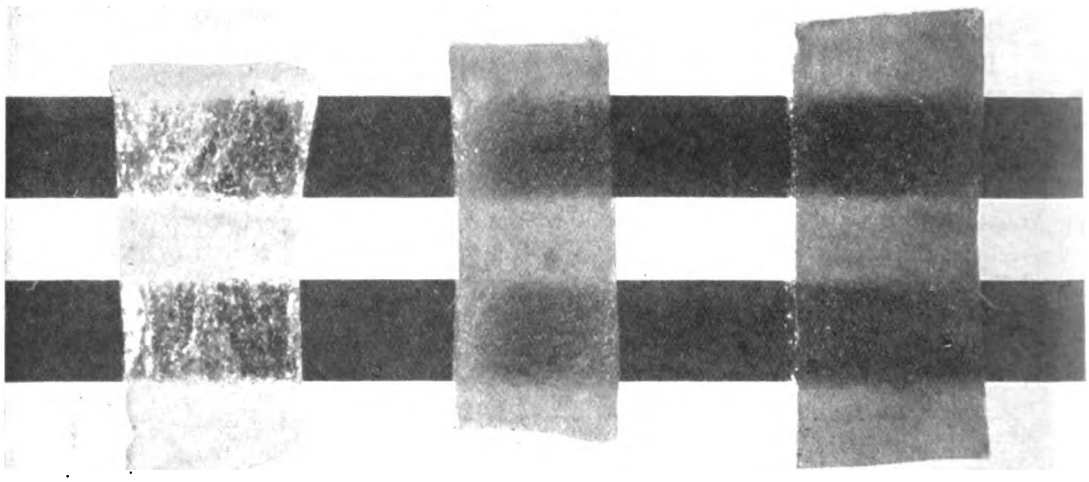


Reflected light



Transmitted light

FIG. 67. Photographs of Blasting Gelatines
(From Report to Parliament of W. Australia by A. E. Mann)

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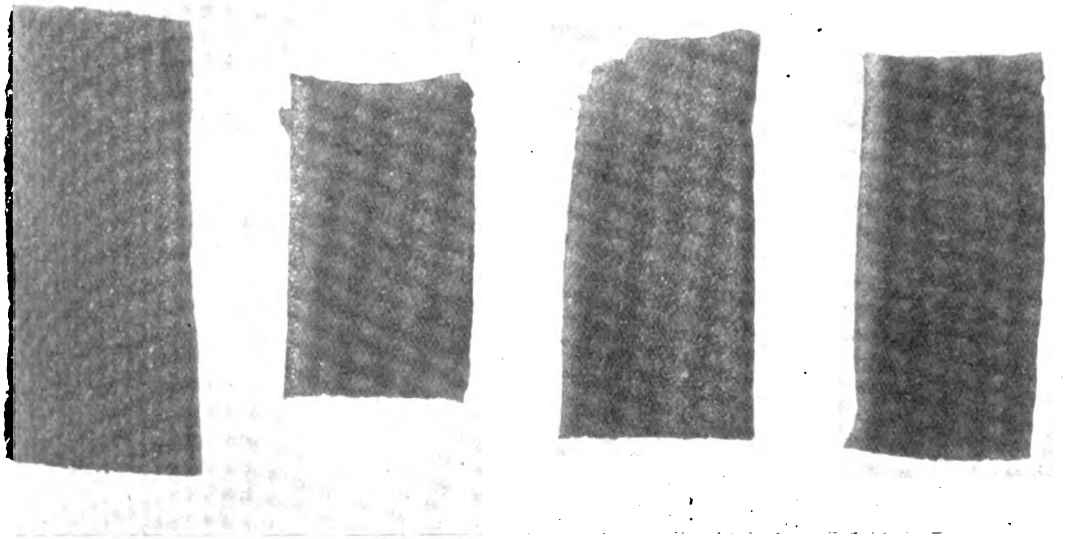

FIG. 68. Photographs of Gelignites
(From Report to Parliament of W. Australia by A. E. Mann)

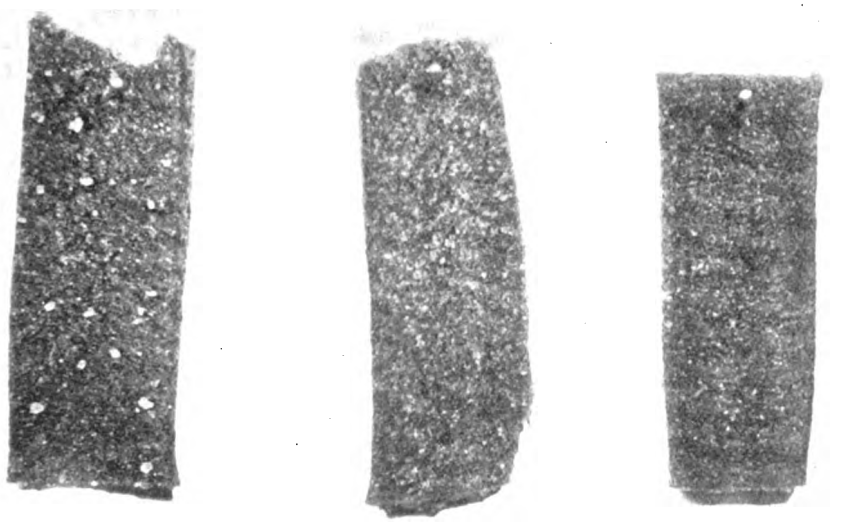

FIG. 69. Photographs of South African Gelignites
(From Report to Parliament of W. Australia by A. E. Mann)

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No. 6 detonator, but gave normal results again when a No. 7 detonator was used.[1] Indeed, it is not easy to produce a collodion cotton, which has the right degree of gelatinizing power and is at the same time sufficiently stable to stand transport through the tropics, to Australia, for instance. In 1909 125,000 lb. of gelignite were condemned in Western Australia alone on chemical grounds.

and stability.

Blasting gelatine may contain anything up to 12 per cent. of collodion cotton, but usually 7 or 8 per cent. To increase its stability 1 or 2 per cent. of calcium or magnesium carbonate may be added, or a fraction of a per cent. of vaseline.

Gelignite.

For most purposes blasting gelatine is considered too expensive and is too violent and local in its action, and consequently explosives are used in which it is rendered milder by the addition of other materials. Gelignite is an explosive, which is very largely employed : it consists of 56 to 63 per cent. of nitro-glycerine thickened with nitro-cotton to a thin jelly and mixed with potassium nitrate and wood-meal, with the addition sometimes of calcium carbonate or mineral jelly.

Gelatine dynamite.

Gelatine dynamite is a mixture very similar to gelignite except that it contains a larger proportion of blasting gelatine : there may be from 70 to 77 per cent. of nitro-glycerine in it.

The following Table shows typical compositions for these three standard gelatinized explosives :

	Blasting Gelatine	Gelatine Dynamite	Gelignite
Nitro-glycerine	91·5	74·5	60·5
Collodion cotton	8	5·5	4·5
Wood-meal	—	4	7
Potassium nitrate	—	15·5	27
Calcium carbonate	0·2	0·2	0·2
Moisture	0·3	0·3	0·8

The object is to make a mixture which shall contain sufficient oxygen to convert the whole of the carbon present into carbon dioxide, so that none of the poisonous carbon monoxide shall be formed to foul the air in mines. It has been shown by Mann (Report to the Western Australian Parliament, 1911)

Wrappers.

that if the paper wrappings on the cartridges are removed very little carbon monoxide is formed ; not more than 2 per cent. of the carbon is converted into this gas, but with the wrappers on from 7 to 14 per cent. is formed. In Great Britain wrappers of parchment paper are used, but on the Continent and America they are often of paraffined paper. A wrapping of metal foil would have far less reducing action, but the finely divided metallic oxide

[1] *A. and E.*, 1912 p. 22.

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would itself have a poisonous action. Impregnation of the paper with nitrates or similar means would make the cartridges considerably more inflammable. For the avoidance of this danger of poisoning with carbon monoxide the most effective means is undoubtedly efficient ventilation of the mines.

Forty per cent. dynamite.

Dynamite No. 4 or 40 per cent. dynamite is a somewhat similar mixture : it contains not more than 39·5 per cent. of nitro-glycerine gelatinized with not less than 0·75 per cent. of nitro-cotton and mixed with sodium nitrate and not less than 16·5 per cent. of dry wood-meal and a little magnesium carbonate. It is sometimes sold under the name of "Farmer's Dynamite" for breaking up sub-soil, making holes for trees and other agricultural purposes, for which an inexpensive explosive is required. It differs from the ordinary American 40 per cent. dynamite in that the nitro-glycerine is gelatinized and a larger proportion of wood-meal is used : the danger of exudation is thus greatly reduced.

American gelatin dynamites.

In America these explosives are called "gelatins" or gelatin dynamites ; according to Hall and Howell[1] they generally have compositions approximating to the following :

Ingredients.	30 per cent. strength	35 per cent. strength	40 per cent. strength	50 per cent. strength	55 per cent. strength	60 per cent. strength	70 per cent. strength
Nitro-glycerine . .	23·0	28·0	33·0	42·0	46·0	50·0	60·0
Nitro-cellulose . .	0·7	0·9	1·0	1·5	1·7	1·9	2·4
Sodium nitrate . .	62·3	58·1	52·0	45·5	42·3	38·1	29·6
Combustible material[2] .	13·0	12·0	13·0	10·0	9·0	9·0	7·0
Calcium carbonate .	1·0	1·0	1·0	1·0	1·0	1·0	1·0
	100·0	100·0	100·0	100·0	100·0	100·0	100·0

A sample of 40 per cent. gelatine dynamite analysed by W. C. Cope was found to contain :

Nitro-glycerine	30·70
Nitro-cellulose	0·88
Sodium nitrate	54·27
Wood-meal	8·58
Sulphur	3·08
Zinc oxide	1·02
Moisture	1·47
	100·00

[1] *Bulletin* 48.

[2] Wood-pulp is used in 60 and in 70 per cent. strength gelatine dynamite. Sulphur, flour, wood-pulp, and sometimes resin are used in other grades. Some manufacturers replace a small percentage of the nitro-glycerine in these grades with an equal amount of ammonium nitrate. This replacement, however, offers little, if any, advantage other than reducing the cost of manufacture.

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Forcite.

The name "Forcite" is also employed sometimes for ordinary gelignites containing potassium or sodium nitrate and wood-meal, but sometimes also for mixtures in various proportions of a thin blasting gelatine with an absorbent having the composition :

Sodium nitrate	76
Sulphur	3
Wood-tar	20
Wood-pulp	1

In Belgium Forcites are manufactured at Baelen-sur-Nèthe, having the following compositions :

	Extra	Supérieur	No. 1	No. 2
Nitro-glycerine	64	64	49	36
Nitro-cellulose	3·5	3	2	3
Sodium nitrate	—	24	36	35
Ammonium nitrate	25	—	—	—
Wood-meal	6·5	8	13	11
Magnesia	1	1	—	1
Rye-bran	—	—	—	14

They are also made with corresponding percentages of potassium nitrate.

French gelatinized explosives.

In France explosives containing nitro-glycerine are excepted from the State monopoly : a large number of different compositions have been authorized for manufacture in the private works. The following are some examples (Chaion) :

	Gomme extra forte	Gommes à la potasse		Gomme à la soude	Gomme B.S.
Nitro-glycerine	92	83	82	83	69·5
Nitro-cellulose	8	5	6	5	5·5
Potassium nitrate	—	10	9	—	24·75
Sodium nitrate	—	—	—	10	—
Wood-meal	—	2	3	2	0·25

	Gelatinée 1A	Gelatinée 1B à la Potasse	Gelatinée 1B à la soude
Nitro-glycerine	64	57·5	57
Nitro-cellulose	3	2·5	3
Potassium nitrate	—	32	—
Sodium nitrate	24	—	34
Wood-meal	8	8	6

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Low-freezing explosives.

Any of the nitro-glycerine explosives can be made with low-freezing nitro-glycerine (*see* Chapter XVI). The methods of incorporating the explosives are the same as if ordinary nitro-glycerine were used. In England, where the winters are not so very severe, reliance is placed rather on keeping the magazines warm than on making additions to the explosive mixtures, but on the Continent and in America a considerable number of such explosives are in use. In Germany and Switzerland several "special" blasting gelatines and gelignites are made containing a percentage of liquid nitro-toluene or other nitro-aromatic compounds, or glycerine esters. In Austria the following are manufactured:

	Dynamit I schwerfrierbar	Dynamit II schwerfrierbar
Nitro-glycerine	55	38·5
Nitro-cellulose	2	1·5
Nitro-toluene	10	8
Wood-meal	8	4·16
Rye flour	—	3·12
Sodium nitrate	24	43·68
Lamp-black	—	0·52
Caput mortuum	0·5	0·52
Sodium carbonate	0·5	—

In America low-freezing dynamites are made which differ from the corresponding "straight" dynamites in that about a quarter of the nitro-glycerine is replaced by nitro-substitution compounds.[1] The Red Cross dynamites made by the E. I. du Pont de Nemours Co. are explosives of this class.

The use of these low-freezing nitro-glycerine explosives diminishes the danger of solidification, but does not overcome it entirely. If the weather be very cold it is still necessary therefore to make use of thaw-houses and warming-pans to prevent accident.

Safety explosives containing nitro-glycerine.

There are a number of explosives made which consist practically of gelignite in which part of the potassium nitrate has been replaced by ammonium oxalate, or a compound containing much water of crystallization such as magnesium sulphate, so as to slow down the explosion and reduce the temperature of the flame. These are mostly used for blasting coal. The most largely used of all the "Permitted Explosives" in Great Britain was at one time Saxonite, made by Nobel's Explosives Co. The consumption in 1907 under the Coal-Mines Regulation Act was 1,721,193 lb. But in 1909 it failed when re-tested in the testing gallery and was removed from the list. It was promptly replaced by Samsonite, in which the limits of composition are considerably narrower, and of which 1,071,143 lb. were used in 1910. Saxonite is still used, however, where permitted explosives are not compulsory and in 1911 the consumption was 135,548 lb.

[1] *See* Hall and Howell, *Bull.* 48, p. 7.

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	Saxonite	Samsonite
Nitro-glycerine	42·5–62	57 – 60
Nitro-cotton	2·5– 5	3 – 4
Potassium nitrate	16 –27·5	17 – 19
Wood-meal	3·5– 8	5 – 7
Chalk	0 – 0·5	– –
Ammonium oxalate	9 –27	12·5-14·5
Moisture		0 – 1·5

Whilst the " Woolwich Test " was in force a number of other explosives very similar to Samsonite were on the Permitted List : Arkite, Rippite, Stowite, Cornish Powder, Swalite, amongst others.

To pass the more severe " Rotherham Test " it has been found necessary to reduce the percentage of nitro-glycerine and increase the amount of nitrate and oxalate. The following are on the Permitted List :

	Arkite, No. 2	Duxite
Nitro-glycerine	31 – 33	31 – 33
Nitro-cotton	0·5– 1·5	0·75– 1·5
Potassium nitrate	26 – 28	– –
Sodium nitrate	– –	27 – 29
Wood-meal	8 – 10	8 – 10
Ammonium oxalate	0 – 2	0 – 2·5
Moisture		
Maximum charge, oz.	40	12
Power (swing of bal. pend.)	2·41"	2·45"

The following have passed the Belgian test and are on the list of " explosifs S.G.P." :

	Dynamite antigrisouteuse V.		Grisoutite
Nitro-glycerine	44	..	44
Cellulose	12	..	12
Sodium sulphate	44	..	—
Magnesium sulphate	—	..	44
Charge limite	650 g.	..	300 g.
Equivalent, dynamite No. 1	359	..	179

There is also Grisoutine II, which is practically the same as Dynamite Antigrisouteuse V.

Carbonite. One of the earliest and most successful safety explosives was Carbonite, which was made by Bichel and Schmidt first about 1885, and after undergoing some modifications gave satisfactory results at the Neunkirchen testing station in 1887. It consists of nitro-glycerine, about 25 per cent., absorbed in wood-meal and mixed with nitrates. The proportion of wood-meal is so high that a large proportion of the carbon is only oxidized to monoxide :

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Nitro-glycerine	25
Potassium nitrate	30·5
Barium nitrate	4
Wood-meal	40
Soda	0·5

The composition has been varied by the substitution of other nitrates for those mentioned, and of rye starch and other carbo-hydrates for wood-meal. The composition has been imitated by many other manufacturers. The following are some of the explosives of this type that passed the Woolwich test :

	Carbonite	Tutol	Kolax
Nitro-glycerine	25–27	24–26	24–26
Potassium nitrate	30–36	32–34½	25–27
Barium nitrate		1– 3	4– 6
Wood-meal	39–42	35–38	29–32
Starch	— —	— —	8–10
Sulphuretted benzene	0– ½	— —	— —
Calcium carbonate	0– ½	— —	— —
Sodium carbonate		— —	— —
Sodium bicarbonate	— —	0– ½	— —
Moisture	4– 8	2– 6	4– 6

There are a number of explosives of this type on the Belgian list of " explosifs S.G.P." :

	Kohlen-carbonite	Minite	Antigel de Sûreté	
Nitro-glycerine	25	25	Nitro-glycerine	25
Potassium nitrate	34	35	Sodium nitrate	20
Barium nitrate	1	—	Dinitro-toluene	15
Flour	38·5	39·5	Ammonium sulphate	5
Tan-meal	1	—	Cellulose	35
Soda	0·5	0·5	Wood-meal	35
Charge limite	900	750	Charge limite	900
Equivalent	501	405	Equivalent	524

Minerite and Colinite antigrisouteuse have the same composition as Kohlen-carbonite, and Securophore III only differs from it in having 1 per cent. wood-meal instead of tan-meal ; its " charge limite " is 850 grams, equivalent to 548 grams Dynamite No. 1. Ingélite is identical with Antigel de sûreté.

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To pass the Rotherham test it has been found necessary to add a cooling agent such as ammonium oxalate or a chloride, or French chalk :

	Cambrite	Essex Powder	Haylite	Nitro-Densite	Pitite 2	Super-Kolax
Nitro-glycerine	22 -24	22-24	25-27	17-19	23 -25	24½-26½
Collodion cotton	—	½- 1½	½- 1½	—	—	—
Potassium nitrate	26 -29	33-35	19-21	—	28 -31	24½-26½
Barium nitrate	3 -4½	—	19-21	24-26	—	4 - 6
Wood-meal	32 -35	—	12-14	4- 6	33 -36	26 -28
Wheat flour	—	32-35	—	—	—	—
Starch	—	—	—	24-27	—	—
Mineral jelly	—	—	6- 8	—	—	—
Ammonium oxalate	7 - 9	—	10-12	—	7 - 9	6 - 8
Ammonium chloride	—	5- 7	—	—	—	—
French chalk	—	—	—	22-24	—	—
Calcium carbonate	0 - ½	—	—	—	—	—
Moisture	3½- 6	2- 5	½- 2½	2- 5	2½- 5	2 - 4
Maximum charge, oz.	30	38	10	28	32	30
Power (swing of bal. pendulum, inches)	1·98	2·17	2·18	1·47	2·15	2·10

The above had all passed the test before March 31, 1913. Between that date and April 7, 1914, four more explosives of this class passed the Rotherham test, viz. : Britonite No. 2, Kynarkite, Tutol No. 2, and Kent Powder.

Some ammonium nitrate explosives also have a small percentage of nitro-glycerine added to render them less insensitive, and to render it possible to compress them to a higher density without making them too difficult to detonate. These are dealt with in Chapter XXIV.

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CHAPTER XXIII

CHLORATE EXPLOSIVES

Chlorate dangers : Sprengel explosives : Prométhée or O3 : Rack-a-rock : Cheddite : Steelite : Silesia : Potassium perchlorate explosives : Permonite : Alkalsit : Polarite : M.B. powder : Ammonium perchlorate explosives : Yonckite : Blastine

THE substitution of potassium chlorate for saltpetre in an explosive mixture increases its power and violence, but also its sensitiveness, especially if it contain sulphur or a sulphide. Hence the early attempts to make gunpowder with chlorate led to disaster (*see* p. 25). Such mixtures are used for percussion caps, and for other purposes where a high sensitiveness is required. They have also been used for the manufacture of coloured lights and other similar fire-works, but in England this is now forbidden. Means have been found, however, to make blasting explosives containing chlorate, which are not more dangerous than other explosives. The perchlorates are much less sensitive than the chlorates, and as they are now manufactured at moderate costs, their use in explosives is extending rapidly. **Chlorate dangers.**

Under ordinary circumstances chlorate of potash, when unmixed with combustible matter, is not dangerous, but on May 12, 1899, a large quantity of it exploded during the progress of a fire at the works of the United Alkali Co. at St. Helens, and did an enormous amount of damage.[1] This led to a more thorough examination of the behaviour of potassium chlorate when heated. Berthelot [2] showed that if it be subjected to a blow combined with sudden intense heat it explodes; he devised the following experiment: A glass tube 25 to 30 mm. in diameter, closed at one end, is supported in a nearly vertical position, and heated in the flame of a large gas-burner, until the lower part has attained a perceptible red heat. A glass rod is drawn out to the thickness of a coarse thread, then introduced into a quantity of pure potassium chlorate, which has been melted in a porcelain crucible, withdrawn and allowed to cool until the salt begins to solidify. The operation is repeated several times until a few decigrammes of solidified salt are accumulated in the form of an oval lump on the end of the glass thread. When the glass tube is quite red, the glass rod is introduced until the potassium chlorate is within about 10 mm. of the bottom, care being taken that it does not touch the tube

[1] *S.R.*, No. 135.

[2] *P. et S.*, vol. x., 1900.

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anywhere. After a short time the chlorate melts and falls, drop by drop, on to the red-hot bottom of the tube. Each drop explodes at the instant that it comes in contact with the glass, producing a very distinct sound and a cloud of white smoke.

Dupré [1] showed that heat alone suffices to explode the chlorate, if it be applied with sufficient suddenness. A bead of potassium chlorate, supported in a loop of thin platinum wire, can be made to explode by heating it rapidly either in a gas flame or by means of an electric current.

Since the St. Helens disaster there have been several other instances in which considerable quantities of potassium chlorate have exploded in the course of conflagrations. On July 27, 1908, an explosion of this sort occurred on the premises of a carrying company in Manchester ; [2] and on July 21, 1910, another at the match-works of Messrs. Bryant and May, at Seaforth, near Liverpool. Although potassium chlorate is not classified officially as an explosive, yet where large quantities are stored they should be kept in an uninflammable building, separate from all combustible materials. The intense inflammability of wood and other organic matter, when impregnated with chlorate, should be borne in mind. The explosibility of chlorate is caused by the fact that heat is liberated when it decomposes into potassium chloride and oxygen. It does not explode with great violence.

Sprengel explosives.

Chlorate explosives may be rendered reasonably safe by adopting the device of Sprengel and issuing the chlorate separately from the combustible matter. The potassium chlorate is made up into porous cartridges, and a liquid combustible is used ; the former is dipped into the latter just before use. These explosives are not allowed in Great Britain, as this dipping operation is considered to constitute a process of manufacture, and consequently may only be carried out in a duly licensed factory.

Prométhée or O 3.

A Sprengel explosive is made in France under the name of " Explosif O 3 " or " Prométhée " ; either the oxygen carrier or the combustible can be varied :

	a	*b*	*c*	
Potassium chlorate .	95	90	80	} Oxygen carrier . 87 per cent.
Manganese dioxide .	5	10	20	

	1	2	
Nitro-benzene . .	50	60	} Combustible . . 13 ,,
Turpentine . .	20	15	
Naphtha. . .	30	25	

[1] *J.S.C.I.*, 1902, p. 217.

[2] *S.R.*, No. 185.

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Any combination of *a*, *b* or *c* with 1 or 2 can be used. The explosive is sold at the price of Fr. 3 per kg.

There is also a factory for Prometheus explosive at Sant. Eusebio, near Genoa, in Italy, where a severe explosion took place on May 10, 1909, killing the manager, head foreman, a customs officer, and eight workmen, and injuring three others.[1]

Rack-a-rock, which has been used very extensively in America, Siberia, and China, consists of cartridges of chlorate of potash, which are dipped just before use into a combustible oil. For this purpose nitro-benzene is used, or "dead oil," which consists chiefly of hydrocarbons from coal tar, or a mixture of the two. The chlorate cartridges are enclosed in small bags of cotton: before use these are placed in a wire basket suspended from a spring balance and dipped into a pail containing the liquid, until a quarter to a third of the weight of the chlorate has been taken up. The chlorate sometimes contains an addition of a few per cent. of iron oxide. Considerable quantities of Rack-a-rock were in store at Port Arthur and Dalny at the commencement of the Russo-Japanese War, and were used in the early operations.[2] **Rack-a-rock.**

The objection has been raised to Sprengel explosives of this sort that the impregnation is not uniform, and the results obtained are consequently unreliable.

Prométhée is similarly issued in the form of compressed cartridges, and the French Government has refused to make it in the form of grains, as the danger of ignition by friction during manufacture and use would be greatly increased.[3] The Government has also refused to issue it ready impregnated with the "combustible," as it would then possess no advantage over Cheddite.[4]

If a charge of Sprengel explosive be fired with a primer of black powder, it should be so made up that admixture is impossible: a compressed pellet of black powder wrapped in impermeable paper may be used for instance. The primer of black powder should be not less than 10 per cent. of the weight of the charge with a minimum of 25 g. (say 1 oz.).

It was discovered by E. A. G. Street, of the firm of Bergés, Corbin et Cie, that the dangerous sensitiveness of chlorate mixtures could be reduced by coating the chlorate with an oily material, such as castor-oil thickened by having a nitro-hydro-carbon dissolved in it.[5] Explosives made on this principle have been examined from time to time by the French Commission des Poudres et Salpêtres, and the manufacture of several has been undertaken by the State.[6] They are called Cheddites from Chedde, the place in Haute Savoie, **Cheddite.**

[1] *A.R.*, 1909, p. 35.
[2] *S.S.*, 1908, p. 19.
[3] *P. et S.*, vol. xv., 1910, p. 130.
[4] *P. et S.*, vol. xv., p. 148.
[5] Eng. Pat. 9,970 and 13,724 of 1897; Ger. Pat. 100,522 of 1897.
[6] *P. et S.*, vol. xi., p. 22; vol. xii., pp. 122, 130; vol. xiii., pp. 29, 144, 282; vol. xiv., p. 33; vol. xv., pp. 212, 247.

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where the above-named firm manufactures chlorates by electrolytic methods. It has been found necessary to keep the proportions of the various constituents within certain limits in order to produce an explosive that shall possess the right degree of sensitiveness and shall not be liable to exude oil. It was also found that the velocity of detonation of Cheddite varies considerably with the density to which it is compressed: with increase of density the velocity of detonation rises until it reaches a maximum and then falls rapidly. This fall is due to the fact that the explosive becomes very insensitive to detonation when the density exceeds a certain critical value, and this difficulty can only be overcome to a slight extent by the use of a stronger detonator. Some of the earlier preparations were found to increase in density on keeping and consequently to diminish in sensitiveness, but this was traced to the use of dinitro-toluene which had been insufficiently purified.[1] The nitro-body should not melt below 60°, else there is danger of exudation.[2] The explosives are easily compressed, and therefore there is danger of diminishing the sensitiveness too much if charges are rammed hard in the bore-hole.

Various attempts have been made to produce a satisfactory Cheddite in which the potassium chlorate is replaced by the cheaper sodium salt, which contains a larger percentage of oxygen, but the mixtures first made were found to be too insensitive, when the density exceeded quite a moderate amount, and very compressible. Moreover, sodium chlorate is very hygroscopic, and when ground gives rise to a great deal of dust, which makes the worker's clothing and similar materials very inflammable.[3] However, it was found that a mixture containing 16 per cent. of dinitro-toluene and no nitro-naphthalene could be fired up to a density of 1·65 and was more powerful than the other types.[4]

04. It has also been found that in potassium chlorate explosives paraffin wax can be substituted for the solution of nitro-compound in castor-oil. A mixture of 90 per cent. potassium chlorate and 10 per cent. paraffin can be fired up to density of 1·38 as compared with 1·48 for type 60, and it is comparatively incompressible, as it requires a pressure of about 40 kg. per sq. cm. to bring it up to the limit density, whereas Cheddite 60 is compressed to its limit density by a pressure of only 2 kg. per sq. cm. A similar explosive containing 89 per cent. sodium chlorate and 11 per cent. paraffin had an equally high limit density, but was very compressible.[5] The following types of chlorate explosive have been approved in France:

[1] *P. et S.*, vol. xiv., p. 33.
[2] *P. et S.*, vol. xiii., p. 144.
[3] *P. et S.*, vol. xiv., p. 26; vol. xv., p. 135.
[4] *P. et S.*, vol. xvi., p. 66.
[5] *P. et S.*, vol. xv., pp. 212, 247.

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	O1 Typ 41	O1 Typ 60	O2	O4	O5
Potassium chlorate . . .	80	80	79	90	—
Sodium chlorate . . .	—	—	—	—	79
Castor-oil	8	5	5	—	5
Mononitro-naphthalene . .	12	13	1	—	—
Dinitro-toluene . . .	—	2	15	—	16
Paraffin	—	—	—	10	—
Price, Fr. per kg. . . .	2·10	2·10	2·30	1·90	—

Manufacture.

In making Cheddite the nitro-compounds are first dissolved in the castor-oil at 60° or 70° C., and the finely powdered dry chlorate is then added gradually, whilst the mass is stirred with a wooden rod. The incorporation lasts about ten minutes. The material is then carried to another building, where it is further mixed on a wooden board in a half-cold condition for another ten minutes, so as to get it in a suitable granular condition. Each particle of chlorate should be entirely coated with the oily mixture. The material is next sifted, and what is too fine is added to a later charge. That which is of the correct size is made into cartridges by ramming it into wooden moulds, from which it is transferred to paper cases. If the explosive contain sodium chlorate, the cases should then be dipped into molten paraffin to prevent the absorption of water. If the percentage of moisture rise above 1 per cent., the explosibility is impaired.

Cheddite is a soft yellowish material of fine grain. In consequence of its plasticity it can easily be compressed. It is generally put up into cartridges 22 cm. long and 2·5 cm. diameter. Cheddite 41 is a slow mild explosive, which splits rocks rather than shatters them. Cheddite 60 is more violent, and the Sodium Clorato Cheddite, O5, still more so. The velocity of detonation of Cheddite 60 was measured by Lheure [1] and found to be 3175 metres per sec., about half of that of picric acid, blasting gelatine, and other very high explosives.

Steelite.

" Steelite " consists essentially of potassium chlorate, the particles of which are enveloped in oxidized resin, which is made as follows : 9 parts of ground colophony are mixed with 1 part of starch, and to this mixture nitric acid of 1·41 specific gravity (67·5 per cent. HNO_3) is added at the ordinary temperature, without the addition of any sulphuric acid. An oxidized yellow amorphous mass is thus formed, which floats on the top of the acid. This is broken up, washed with water, dried at a moderate temperature, and ground up. It is not explosive without the addition of chlorate, and only burns with

[1] *P. et S.*, vol. xii., p. 117.

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difficulty. It is mixed with the ground chlorate and other constituents in a drum with lignum vitæ balls. The mixture is spread on a zinc sheet in quantities of 1 to 5 kg. and sprinkled with methyl-alcohol, whilst it is raked about, so that a paste or dough may not be formed. It is kept in gentle motion with a wooden tool until it is dry.

Several samples of Steelite were examined by the French Commission des Substances Explosives, but it was decided not to undertake its manufacture on the ground that it possessed no advantages over Cheddite, than which they were more sensitive and less dense.[1] Colliery Steelite containing a small percentage of castor-oil passed the Woolwich test for safety explosives and was formerly on the English "permitted list."

Silesia.

In Germany this explosive is called "Silesia": unoxidized resin is apparently used in it sometimes, and to make it pass the Continental tests for safety explosives a considerable proportion of sodium chloride is added. The following are some of the compositions that have been made:

	Colliery Steelite	No. 3	No. 5	Silesia IV 22	Silesia 4
Potassium chlorate . .	72·5–75·5	75	79·2	70	80
Oxidized resin . . .	23·5–26·5	25	15·8	8	20
Castor-oil . . .	0·5– 1	—	—	—	—
Aluminium . . .	—	—	5	—	—
Sodium chloride . .	—	—	—	22	—
Moisture . . .	0 – 1	—	—	—	—

The Silesia explosive has a large excess of chlorate, and the gases produced contain 14·2 per cent. of free oxygen.[2]

Chlorates should never be mixed with ammonium salts, as ammonium chlorate would be formed, and this is liable to explode spontaneously. Mixtures with picric acid or trinitro-cresol also should not be made, as they are very sensitive.

POTASSIUM PERCHLORATE EXPLOSIVES

The perchlorates possess the advantage over the chlorates, that they are more stable and less sensitive, although they contain a larger proportion of oxygen. Consequently explosives containing perchlorates do not require to have each particle encased in fatty matter, as is the case with chlorate explosives.

[1] *P. et S.*, vol. xv., p. 181.

[2] *See* Escales, *Chloratsprengstoffe*, 1910, p. 143.

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Explosives containing potassium perchlorate and ammonium nitrate together with trinitro-toluene, starchy matter and wood-meal, are made by the Spregstoff-A.-G. Carbonit under the name of "Permonite." One of these compositions was formerly on the English "permitted list," and another is on the Belgian list of Explosifs S.G.P. Gesteins-Permonit is used in potash and ore mines. The following are the compositions, together with other particulars as stated by the makers: **Permonite.**

	Permonit I or Gesteins-Permonit	Permonite S.G.P.	Permonite (Permitted List)
Potassium perchlorate	30	24·5	31 -34
Nitro-glycerine	—	6	3 - 4
Collodion cotton	—	—	0·5- 1
Ammonium nitrate	40	29	39 -43
Sodium nitrate	7	—	—
Trinitro-toluene	15	7	11 -13
Sodium chloride	—	25	—
Flour	4	4	—
Starch	—	—	5 - 9
Wood-meal	3	3	1·5- 3·5
Jelly	1	1	—
Moisture	—	—	0 - 2·5
Influence test	70 mm.	100 mm.	80 mm.
Trauzl test	320 c.c.	205 c.c.	365 c.c.
Velocity of detonation	3470 m/sec.	2326 m/sec.	—
Sensitiveness, 2 kg. weight	70 cm.	80 cm.	20 cm.
„ 10 kg. „	5	10	—

The "charge limite" of Permonite S.G.P. is 900 g., equivalent to about 570 g. of dynamite No. 1.

The "jelly" is a mixture of 1 part glycerine and 3·5 parts gelatine: the influence test consists in ascertaining the distance over which detonation is conveyed from one 30 cm. cartridge to another lying on the ground.

Another very similar explosive made in Germany is Alkalsit. Polarite, a non-freezing explosive of high power, is used in England as a substitute for Gelignite. **Alkalsit. Polarite.**

Four explosives containing potassium perchlorate have passed the Rotherham test, and are on the English Permitted List. They differ from the Permonites in that they contain a larger proportion of nitro-glycerine and wood-meal, and the ammonium nitrate has been replaced by oxalate, so that they are not hygroscopic. The result is that instead of an excess of available oxygen they contain a slight deficit.

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	Dynobel	Neonal	Ajax powder	Swale powder
Potassium perchlorate	26 -28	36 -38	36·5-38·5	36·5-38·5
Nitro-glycerine	31·5-33·5	20 -22	21·5-23·5	18 -20
Collodion cotton	0·5- 1	0·5- 1·5	0·5- 1	0·5- 1·5
Di- and trinitro-toluene	—	0 - 0·4	3 - 4	3 - 5
Ammonium oxalate	28·5-30·5	24 -26	24 -26	27 -29
Wood-meal	8·5-10·5	14 -16	9·5-11·5	8 -10
Moisture	0 - 1·5	0 - 2	0 - 1·5	0 - 2
Maximum charge	22 oz.	16 oz.	12 oz.	20 oz.
Power (swing of bal. pend.)	2·61″	2·56″	2·69″	2·50″

The addition of nitro-toluenes renders the explosives less liable to freeze.

M.B. powder. A different type of perchlorate explosive is represented by M.B. Powder (Modified Black), which consists of black powder in which part of the saltpetre has been replaced by potassium perchlorate. It is made in much the same way as Safety Blasting Powder was, that is to say the ingredients, after a preliminary mixing, are incorporated together in a steam-jacketed pan. On November 25, 1911, a severe fire occurred in the house where this operation was being carried out, whereby three men were killed and one was injured. It was ascribed to friction on dry caked material in the steam-heated incorporator.

AMMONIUM PERCHLORATE EXPLOSIVES

As a constituent of an explosive, ammonium perchlorate possesses the advantage that it contains a high proportion of available oxygen and only produces gaseous products, but unfortunately these include the poisonous gas hydrogen chloride. The formation of this can be prevented by adding an equivalent quantity of some substance such as sodium nitrate, which will yield a base to combine with the chlorine. In 1906 the French "Commission des Substances Explosives" investigated two Cheddites containing ammonium perchlorate, and although it was decided not to undertake their manufacture some of the experiments are instructive.[1] The explosives had the compositions :

	I.	II.
Ammonium perchlorate	82	50
Dinitro-toluene	13	15
Sodium nitrate	—	30
Castor-oil	5	5

[1] *P. et S.*, vol. xiv., pp. 192, 206.

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No. I burns with dangerous rapidity when ignited, but II is quite safe in this respect. Fabrics impregnated with ammonium perchlorate are more inflammable than when potassium chlorate is used, but not so much so as with sodium chlorate. Ammonium perchlorate is a mild explosive by itself, but is

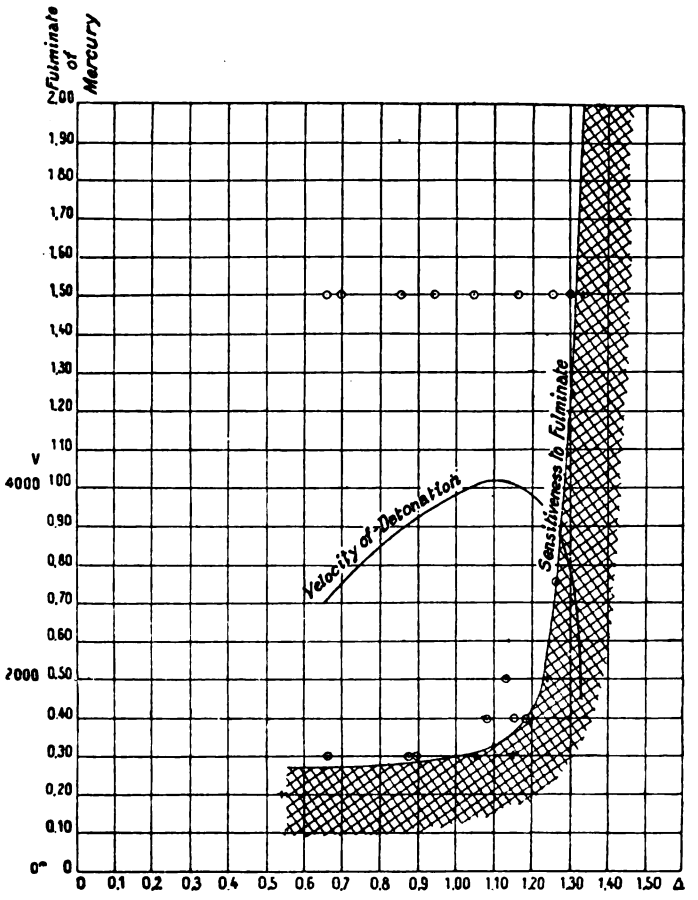

FIG. 70. Detonation of Ammonium Perchlorate Cheddite at Different Densities

only exploded with difficulty and incompletely : at ordinary temperatures it is stable, but at 150° decomposition sets in after a time and proceeds according to the equation : $NH_4ClO_4 = Cl + O_2 + N + 2H_2O$ (gaseous) + 38·3 cal. The reaction is apparently auto-catalytic.[1] It is very important that ammonium perchlorate be kept quite separate from the chlorates of sodium and potassium, as dangerous double decompositions are liable to occur. Ammonium perchlo-

[1] *See* Girard and Laroche, *Moniteur scientifique*, April 1909 ; *S.S.*, 1910, p. 134.

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rate has about the same degree of sensitiveness to impact as picric acid: a 5 kg. weight falling 50 cm. causes explosion sometimes. As in the case of other Cheddites the velocity of detonation rises with increase of density to a maximum, after which it falls in consequence of the diminution of the sensitiveness to detonation. This is clearly shown by the curves in Fig. 70, which gives the velocities of detonation and the weights of fulminate required to detonate explosive I, when loaded into cartridges at different densities.

Yonckite. A number of explosives of this type are made in Belgium under the name of Yonckites. One of these, Yonckite 10bis, is on the Belgian list of Explosives S.G.P.; it has the composition:

Ammonium perchlorate	25
Ammonium nitrate	30
Sodium nitrate	15
Trinitro-toluene	10
Sodium chloride	20

The " charge limite " is 900 g., equivalent to 540 g. Dynamite No. 1.

Blastine. An explosive, which is now being used very extensively is Blastine, in which ammonium perchlorate and sodium nitrate are mixed with the combustible matters, dinitro-toluene and paraffin wax.

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CHAPTER XXIV

AMMONIUM NITRATE EXPLOSIVES

Favier explosives : Grisounites : Ammonals : Grisoutine

ATTENTION was first drawn prominently to the use of ammonium nitrate as a constituent of explosives in consequence of the numerous explosions of coal damp and dust in mines. The low temperature of explosion of mixtures containing large proportions of ammonium nitrate indicated its use for this purpose. In 1884 and 1885 Favier took out patents for mixtures of ammonium nitrate with mononitro-naphthalene, paraffin and resin.[1] The manufacture was soon afterwards undertaken by the French Government and is still continued under the name of Explosifs N, or Explosifs Favier, or Poudres de sureté. **Favier explosives.**

The ammonium nitrate is first dried and then ground in a mill, the pan of which is heated by steam or hot water. The nitro-naphthalene is then added, and the incorporation is carried on for an hour or two in a warm dry room. The mass is then allowed to cool and is ground to a powder, after which it is loaded into cartridges. In some cases the cartridges are formed under considerable pressure, but in that case it is necessary to remove the core and introduce a primer of the powdered explosive, because if the density be too high, the explosive is very difficult to detonate. In other cases the cartridges are formed under a moderate pressure only, such as that produced by an Archimedean screw working against a slight resistance. The cartridges are contained in wrappers of metal-foil or paper rendered waterproof by dipping in a bath of paraffin-wax. According to the German regulations for the manufacture of ammonium nitrate explosives the temperature of the wax bath must not exceed 100° C. Waterproofing is absolutely necessary because ammonium nitrate is extremely hygroscopic. **Manufacture.**

The composition of the Favier explosives made in France has been varied from time to time. The following were the authorized compositions of Explosifs N according to the *Journal Officiel* of October 31, 1910 : **Explosifs N**

[1] Ger. Pat. 31,411 of May 27, 1884 ; Eng. Pat. 2139 of February 16, 1885.

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	1a, bis	1b, bis	1c, bis	2	3	4
Ammonium nitrate	95	91·5	87·4	—	15	90
Sodium nitrate	—	—	—	80	58	—
Potassium nitrate	—	—	—	—	—	5
Mononitro-naphthalene	—	—	—	20	—	—
Dinitro-naphthalene	—	8·5	12·6	—	—	—
Trinitro-naphthalene	5	—	—	—	27	5
Price, Fr. per kg.	2·35	2·45	2·55	1·15	1·90	2·25

Grisounite.

Of these N1a, bis and N4 are intended for use in the coal-seams as they have theoretical temperatures of explosion of 1500° or less; they are called "Grisounites couches," and are coloured with methylene green B. N1a is but little used now. The others, which have theoretical temperatures of explosion of 1900° or less, are intended for use in the rocks in coal-mines, and are known as "Grisounites roches." N2 is not an ammonium nitrate explosive. N3 gives its maximum velocity of detonation when compressed to a density of 1·38 if dry; it is then 3800 metres per second. The limit density, beyond which it cannot be detonated completely, is 1·4. If damp the limit density is reduced. It is put up in cartridges with a density of 1·2, and then has a velocity of detonation of about 3200 metres per second. The other explosives of the type have lower limit densities.[1]

The following are some of the principal explosives that passed the Woolwich test and so obtained a place on the Permitted List:

	Ammonite	Westfalite		Bellite		Roburite
		1	2	1	3	3
Ammonium nitrate	87–89	94–96	90–92	82–85	92–95	86–89
Potassium nitrate	—	—	3– 5	—	—	—
Dinitro-naphthalene	11–13	—	—	—	—	—
Dinitro-benzene	—	—	—	15–18	5– 8	9–13
Chloro-naphthalene	—	—	—	—	—	0– 2
Resin	—	4– 6	4– 6	—	—	—
Moisture	0– ½	0– ½	0– ½	0– ¾	0– ¾	0– ½

In order to pass the Rotherham test, in which the explosive is fired without stemming into the gas mixture, the compositions have had to be modified somewhat:

[1] *P. et S.*, vol. xvi, pp. 1, 63.

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	Westfalite No. 3	Kentite	Expedite	Supercurtisite
Ammonium nitrate	58–61	32·5–35·5	33–36	37–40
Potassium nitrate	13–15	32–35	32–34	28–31
Trinitro-toluene	4–6	14–16	11–13	9–11
Ammonium chloride	20–22	16–18	19–21	21–23
Moisture	0–1	0–2	0–1·5	0–2
Maximum charge, oz.	12	18	32	16
Power (swing of bal. pend.)	2·55″	2·64″	2·62″	2·71″

New Fortex differs from Expedite only in containing "amido-compound" instead of trinitro-toluene. Its power is practically the same, but the maximum charge is only 10 oz.

	Dreadnought powder	Ammonite No. 1	Nationalite	Negro powder
Ammonium nitrate	73–77	73–77	64–68	55–58
Sodium nitrate	14–17	--	—	—.
Trinitro-toluene	3–5	4–6	14–16	14–16
Ammonium chloride	4–6	—	—	--
Sodium chloride	—	19·5–21·5	18·5–20·6	26–29
Graphite	—	—	—	0·5–1
Moisture	0–1	0–1	0–1	0–1
Maximum charge, oz.	32	24	12	20
Power	2·05″	2·42″	2·92″	2·21″

Dreadnought Powder contains also up to 0·1 per cent. red oil, and Negro Powder a similar amount of colouring-matter.

In Belgium the following are on the list of Explosifs S.G.P. :

	Densite 4	Favier 3 bis	Densite 3	Poudre blanche Cornil 1 bis	Favier 2 bis	Fractorite B	Minolite antigrisouteuse
Ammonium nitrate	18	60	74	77	77·6	75	72
Potassium nitrate	45·5	11	—	1	—	—	—
Sodium nitrate	—	—	22	—	—	—	23

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	Densite 4	Favier 3 bis	Densite 3	Poudre blanche Cornil 1 bis	Favier 2 bis	Fractorite B	Minolite antigrisouteuse
Potassium permanganate	—	0·5	—	—	—	—	—
Lead chromate	—	—	—	1	—	—	—
Trinitro-toluene	19	8·5	4	—	—	—	3
Trinitro-naphthalene	—	—	—	—	—	—	2
Dinitro-naphthalene	—	—	—	3	2·4	2·8	—
Flour	—	6	—	—	—	—	—
Ammonium oxalate	—	—	—	—	—	2·2	—
Alum	—	5	—	—	—	—	—
Ammonium chloride	17·5	4	—	18	20	20	—
Barium carbonate	—	5	—	—	—	—	—
Charge limite g.	850	750	700	500	500	450	400
Equivalent, Dyn. No. 1	549	452	310	305	293	286	236

The following are the results given by some German safety explosives tested at the Gelsenkirchen testing station:[1]

	Roburit		Neu-Westfalit	Glückauf	
	II[2]	III		AI	AIII
Ammonium nitrate	71·5	55	70·3	70·4	82·7
Potassium nitrate	5	9·5	—	10	—
Potassium permanganate	0·5	0·5	—	—	—
Dinitro-benzene	—	—	—	1	1
Dinitro-toluene	—	—	10·9	—	—
Trinitro-toluene	12	12	—	—	—
Wood-meal	—	—	—	6·4	11·5
Flour	6	6	2	—	—
Fennel (?)	—	—	—	7·2	—
Ammonium chloride	—	5	—	—	—
Sodium chloride	5	7	16·8	—	—
Magnesite	—	5	—	—	—
Copper oxalate	—	—	—	5	4·8
Limit charge, g.	350	650	540	400	450
Trauzl test, c.c.	325	257	309	312	341

[1] *S.S.*, 1907, p. 13.

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Other German Favier explosives are:

	Dahmenit	Dorfit		Aldorfit	Fulmenit	Wetter-Fulmenit
		I	II			
Ammonium nitrate	91·3	65	61	81	86·5	76·5
Potassium nitrate	—	5	5	—	—	—
Potassium bichromate	2·2	—	—	—	—	—
Gun-cotton	—	—	—	—	4	4
Trinitro-toluene	—	6	15	17	5·5	5·5
Paraffin oil	—	—	—	—	2·5	2·5
Rye flour	—	4	4	2	—	—
Naphthalene	6·5	—	—	—	—	—
Charcoal	—	—	—	—	1·5	1·5
Sodium chloride	—	20	15	—	—	10
Limit charge, g.	—	532	300	—	—	—
Trauzl test, c.c.	—	172	219	—	—	—

Of these Aldorfit and Fulmenit are not intended for use in dangerous coal-mines. Dorfit and Wetter-Fulmenit differ from them in containing considerable percentages of sodium chloride which reduces the temperature of explosion. Monachit resembles Dorfit and Aldorfit.[1]

Under the name of Raschit, Raschig has recently introduced a number of explosives containing ammonium nitrate and highly soluble organic substances such as ammonium mononitro-cresol-sulphonate, sodium cresol-sulphonate, or the residue obtained in the manufacture of wood cellulose. The incorporation is carried out by dissolving the constituents in water and evaporating the solution rapidly on a rotating steam-heated drum.

The Austrian Government manufacture as safety explosives:

	Dynammon	Wetter-Dynammon
Ammonium nitrate	87–88	94
Potassium nitrate	—	2
Charcoal	12–13	4
Density	0·9	0·85

Ammonal. The idea of utilizing the great amount of heat energy that is liberated in the oxidation of aluminium has formed the subject of patents taken out by G. Roth, of Vienna,[2] and mixtures of ammonium nitrate, aluminium, and other substances have been brought on the market mostly under the name

[1] *See S.S.*, 1909, p. 106.

[2] Ger. Pat. 172,327 of June 28, 1900; Eng. Pat. 16,277 of September 13, 1900.

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of Ammonal. In spite of the high temperature produced by the oxidation of aluminium three of these compositions were able to pass the Woolwich test.

	Ammonal B	Ripping Ammonal	St. Helens powder
Ammonium nitrate	93–95·5	84–87	92–95
Aluminium	2·5–3·5	7–9	2–3
Charcoal	2–3	2–3	—
Trinitro-toluene	—	—	3–5
Potassium bichromate	—	3–4	—
Moisture	0–1	0–1	0–1

For safety in coal-mines it is necessary to keep down the percentage of aluminium. In Ripping Ammonal the safety is increased by the addition of potassium bichromate, and consequently the proportion of aluminium can be increased.[1] For ordinary blasting purposes compositions such as the following are used :

Ammonium nitrate	72	..	47
Aluminium	25	..	22
Charcoal	3	..	1
Trinitro-toluene	—	..	30

Ammonal is an explosive of considerable power.[2] The velocity of detonation of an Ammonal was found by Bichel to be 3450 metres per second.

Two explosives of this class are manufactured in Germany under the name of Gesteins-Westfalit B and C: B contains dinitro-benzene and C dinitro-toluene. Roth's Ammonal patent has been contested in Germany, but on June 24, 1911, it was confirmed by the Courts.

In Switzerland an explosive similar to Gesteins-Westfalit C is made under the name of Telsit A.

The Ammonals manufactured at the Felixdorf Powder Works in Austria (G. Roth A.G.) have the following composition :

	a	b	c	d
Ammonium nitrate	80·75	90	88	80
Aluminium	15	4	8	18
Charcoal	4·25	6	4	2

[1] Eng. Pat. 16,514 of 1905, W. Macnab and Ammonal Explosives Ltd.

[2] *See* Bichel, *Ang.*, 1905, p. 1889 ; also *S.S.*, 1906, p. 26 ; Rudolph, *Kriegstechnische Zeitschrift*, 1907, p. 233 ; Bravetta, *S.S.*, 1906, p. 199, and 1907, p. 13.

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Ammonal is not allowed to be used in fiery mines, but only where dynamite would be permitted.[1]

The effect of adding aluminium to an ammonium nitrate explosive was investigated by Bichel,[2] who obtained the following results :

Explosive :	Dynammon	Ammonal
Ammonium nitrate	95·5	72·0
Aluminium	—	23·5
Charcoal (red)	4·5	4·5
Density	·865	·900
Velocity of detonation, m/sec.	3380	3450
Heat of explosion in calorimeter	727·0	1600·5 Cal.
Products of explosion :		
Carbon dioxide	13·14	7·00
Carbon monoxide	—	4·57
Water	49·60	14·14
Oxygen	2·60	—
Nitrogen	34·66	28·47
Methane	—	0·25
Hydrogen	—	1·19
Aluminium oxide	—	44·38
Volume of permanent gas, N.T.P.	360	418 litres/kg.
„ water vapour	617	176
Total volume	976	594
Explosion pressure (calculated)	6338	9425 kg/sq.cm.
Trauzl test	250	329 c.c.

Bichel considers that the results of the Trauzl test are misleading, because the great heat of the explosion in the case of the aluminium explosive melts the surface of the lead and so makes the apparent expansion of the hole greater. The Felixdorf Powder Works contend, however, that ammonal is a very powerful explosive: when exploded on top of a small lead cylinder, it compresses it considerably more than a gelignite containing 65 per cent. nitro-glycerine, and it breaks up a shell more than an equal weight of cast picric acid.[3]

Grisoutine.

The only explosives allowed in the more dangerous French coal-mines, in addition to the Grisounites, are the Grisoutines, which consist of ammonium nitrate mixed with blasting gelatine. As the State monopoly does not extend to explosives containing nitro-glycerine, these are made by private firms, but the compositions are regulated by the State. In 1911 the "Commission des Substances Explosives" resolved that the compositions should be unified as follows :

[1] *S.S.*, 1910, p. 54. [2] *Ang.*, 1905, p. 1889.

[3] *S.S.*, 1906, p. 26. *See also* Rudolph, *Kriegstechnische Zeitschrift*, 1907, p. 287 ; *S.S.*, 1907. p. 314.

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	Couche	Couche au Salpêtre	Roche	Roche au Salpetre
Nitro-glycerine	12·0	12·0	29	29
Collodion cotton	0·5	0·5	1	1
Ammonium nitrate	87·5	82·5	70	65
Potassium nitrate	—	5·0	—	5

The calculated temperatures of explosion of the Grisoutines Couche are below 1500°, those of the Grisoutines Roche below 1900°. The addition of 5 per cent. saltpetre instead of the same quantity of ammonium nitrate has been found to increase the safety, probably because the potassium compounds formed are dissociated and vaporized at the temperature of explosion, and afterwards give up again the energy they have absorbed, so that the effect is not very much less. It is estimated that the explosives with 5 per cent. potassium nitrate are about 5 per cent. weaker than the others.[1]

A number of explosives similar to these passed the Woolwich test and were formerly on the Permitted List. Monobel, one of the principal ones, had the composition :

Nitro-glycerine	9–11
Ammonium nitrate	78–82
Wood-meal	8–10
Moisture	0·5–2·5

To pass the more severe Rotherham test it has been found necessary in most cases to add sodium chloride or ammonium oxalate :

	Melling powder	Superexcellite No. 2	Sunderite	Pitsea powder No. 2
Nitro-glycerine	4–6	3·5–5	8–10	6–7
Ammonium nitrate	51–55	73·5–77	50·5–54·5	53·5–56·5
Potassium nitrate	—	6·5–8	—	9–11
Sodium nitrate	11–13	—	—	—
Potassium perchlorate	—	—	8–10	—
Wood-meal	3–5	2–4	7–9	8–10
Trinitro-toluene	5–7	—	—	—
Ammonium oxalate	18–20	9–11	19–21	17·5–19·5
Moisture	0–2	0–1·5	0–2	0–2
Maximum charge, oz.	12	10	16	8
Power	2·62″	2·74″	2·66″	2·64″

[1] *See P. et S.*, xv., pp. 189, 190.

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	Superite	Syndite	Monarkite	Monobel No. 1	Permon powder
Nitro-glycerine	3·5–4·5	10–12	11–13	7·5–9·5	11–13
Collodion cotton	—	0·1–0·3	0–0·5	—	0·2–0·5
Ammonium nitrate	80–84	45–49	48–51	66–70	54–57
Potassium nitrate	9–11	—	6·5–8·5	—	—
Sodium nitrate	—	7–9	—	7–9	0·5–1·5
Wood-meal	—	2–5	3–5	—	—
Starch	2–5	—	—	—	8·5–10·5
Sodium chloride	—	26–28	26–28	14–16	16–18
Glycerine	—	2–5	—	—	3–5
Mineral jelly	—	—	1·5–2·5	—	—
Moisture	0–2	0–2	0–2	0–2	0–3
Maximum charge, oz.	10	40	26	10	18
Power	2·53″	2·22″	2·67″	2·81″	2·57″

On the Belgian list of Explosifs S.G.P. are the following :

	Fractorite D	Flammivore III	Ammon-carbonite
Nitro-glycerine	4	6	4
Ammonium nitrate	75	70	82
Potassium nitrate	—	—	10
Sodium nitrate	10	—	—
Ammonium oxalate	7	—	—
Carbohydrates	4	8	4
Ammonium sulphate	—	9	—
Barium sulphate	—	7	—
Charge limite	700	650	300
Equivalent, Dyn. No. 1	420	382	191

There is also Colinite antigrisouteuse B, which is a gelignite containing ammonium nitrate and other constituents :

Nitro-glycerine	25
Collodion cotton	1
Ammonium nitrate	20
Potassium perchlorate	6
Trinitro-toluene	12
Cellulose and flour	29
Magnesium sulphate	7
Charge limite	800
Equivalent, Dyn. No. 1	460

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Of German Grisoutines the following may be mentioned :

	Salit	Tremonit	Donarit	Ammon-karbonit I
Nitro-glycerine	11·8	—	3·8	4·0
Dinitro-glycerine	—	33·0	—	—
Collodion cotton	0·5	1·0	0·2	0·2
Ammonium Nitrate	53·6	26·5	80·0	80·3
Potassium nitrate	—	—	—	5·0
Dinitro-toluene	8·5	—	—	—
Trinitro-toluene	—	2·5	12·0	—
Sodium chloride	23·1	25·0	—	—
Carbohydrates	2·5	12·0	4·0	4·5
Coal dust	—	—	—	6·0
Charge limite	660	730	130	300
Trauzl test	287	268	450	355

	Astralit	Wetter-Astralit
Nitro-glycerine	4	4
Ammonium nitrate	84·5	74·5
Sodium chloride	—	10
Trinitro-toluene	7	7
Wood-meal	1	1
Charcoal	1	1
Paraffin oil	2·5	2·5

Gelatine-Westfalit is a low-freezing safety nitro-glycerine explosive containing not more than 50 per cent. dinitro-chlorhydrine and 5 per cent. nitro-glycerine gelatinized with a small proportion of collodion cotton, and containing ammonium nitrate, not more than 10 per cent. saltpetre, together with hydrocarbons, vegetable meal, neutral salts and nitro-compounds.

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CHAPTER XXV

THE CHOICE OF A HIGH EXPLOSIVE

For hard rock : Tonite : Soft rock : Blasting under water : Agriculture : Hail-storms : Dimensions of cartridges : Statistics : Military blasting : Gun-cotton : Picric acid : Trinitro-toluene : Smokeless powder : Submarine mines : Shell : Shrapnel : Common shell : Armour-piercing shell : High explosive shrapnel : Grenades : Flying machines : Tracers : Products from explosives : Carbon monoxide : Nitrogen oxides : Acrolein, prussic acid, nitro-glycerine : Hydrochloric acid : Hydrogen sulphide

THE principal factors which govern the choice of a blasting explosive for a specific purpose are the power, velocity of detonation, density and price. The sensitiveness, stability, and the nature of the products formed must also be taken into account in some cases. These different factors assume varying degrees of importance according to the circumstances. For blasting very hard rock, such as gold quartz, a very brisant explosive is required; and on account of the expense of drilling, it must give a maximum of power in a minimum of volume. Blasting gelatine possesses all these qualities in a high degree, provided that it be fired with a very powerful detonator or primer, but if fired with a detonator of only moderate power, its velocity of detonation is only about 1500 metres per second instead of about 7000. To a less extent this also applies to gelignite and other similar gelatinized nitro-glycerine explosives, and accounts for the preference given in America and South Africa to non-gelatinized mixtures, which are not looked upon with favour by the authorities in England on account of the danger of exudation. It would seem that these very hard rocks would be blasted best with a charge of blasting gelatine provided with a primer of non-gelatinized nitro-glycerine explosive, such as American straight dynamite or Ligdyn.

Hard rock.

A high explosive that was much used formerly is Tonite, which consists of gun-cotton mixed with a nitrate, mostly that of potassium, and compressed into blocks or cylinders. It sometimes contains some trinitro-toluene. A Belgian Tonite with which Watteyne carried out some experiments [1] had the composition :

Tonite.

Gun-cotton	53·0
Barium nitrate	37·6
Sodium nitrate	9·4

Tonite has now been replaced to a large extent by other explosives.

[1] *S.S.*, 1913, p. 427.

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Soft rock. With softer rocks the expense of drilling is less; the bore-hole can consequently be made larger, and the density and power of the explosive are not so important. In Great Britain gelignite is the high explosive most used for this class of work, but ammonium nitrate and chlorate explosives are also much employed. If it be desired not to break up the material too much, a very high velocity of detonation is a disadvantage, and care should be taken not to overcharge the holes. For soft material such as coal, which it is not desired to break up too much, a mild explosive is best. Hence the popularity of Bobbinite. When the condition of the material is unimportant, as in the case of carnallite in the German potash mines, the principal consideration is to obtain the maximum power for the money spent. Sprengsalpeter is therefore much used for this purpose. Its slow rate of explosion is said, moreover, to be of advantage.

Blasting under water. For blasting rock under water a brisant explosive is required, and the cartridges should be thoroughly waterproofed unless the explosive contains a considerable percentage of gelatinized nitro-glycerine. In cold weather there is great danger of the nitro-glycerine freezing after the cartridges have been placed in the bore-hole under water. Extra strong detonators should therefore be used. Under water an explosive produces considerably less effect upon the rock than it would on land, for the pressure of the surrounding water lends support to the material that is being blasted.[1]

Agriculture. Of late years there has been a great increase in the use of explosives for agricultural purposes: for breaking up hard sub-soil, removing tree-trunks, digging ditches, etc. If the charge can be tamped well, non-detonating explosives, such as blasting powder, would probably be the most economical on account of their low price, and the fact that the cost of the detonator is saved. In many cases, however, the ground is so unresistant that it is better to use a detonating explosive.

Hailstorms. Some years ago there was much talk of preventing hailstorms by bombarding the sky with high explosives, the idea being that the shock would cause the moisture to be precipitated as rain instead of hail. Much money was spent on endeavours of this sort in the vine districts of Styria, Italy, and France, and there were loud claims of great successes, but later on the enthusiasm waned and died: in fact many of the previous advocates of the shooting came to the conclusion that it actually made the hailstorms worse. Be that as it may, an experimental inquiry carried out on a very large scale on behalf of the Italian Government led to the conclusion that the shooting did absolutely no good.[2]

Dimensions of cartridges. In consequence of the large number of different weights and sizes of cartridge demanded by different consumers Capt. Lloyd at the 7th Inter.

[1] *See* Hall and Howell, *Bull.* 48.

[2] *See* Blaserna, *P. et S.*, vol. xiv, p. 76.

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Cong. Appl. Che. (1909) proposed that they should only be made of the following dimensions:

	Weight	
	Grammes	Ounces
No. 2	50	2
,, 3	75	3
,, 4	100	4
,, 6	150	6
,, 8	200	8
,, 16	400	16

Size	Diameter mm. (approx.)	Diameter in.	
2	22	$\frac{7}{8}$	Common size for gelatinous explosives.
3	33	$1\frac{1}{4}$	To take the place of $1\frac{1}{8}$ in. and $1\frac{3}{8}$ in. the commonest sizes for granular and bulky explosives.
4	44	$1\frac{3}{4}$	For soft rocks and coal.
5	55	$2\frac{3}{16}$	For heavy charges.

Using the weight as numerator and the size as denominator the most common cartridges of gelatinous explosives would be: 2/2, 3/3, 4/3, 6/4, 8/4, and more rarely: 3/2, 2/3, 4/4, 8/5, 16/5. For granular and bulky explosives the commoner dimensions would be: 2/3, 3/3, 4/3, 4/4, 6/4, and occasionally: 6/3, 8/4, 6/5, 8/5.

To a large extent this proposal has been put into execution. Since March 31, 1913, in certain mines in the United Kingdom cartridges are only allowed to be used if they are of the diameter $\frac{7}{8}$, $1\frac{1}{4}$, $1\frac{7}{16}$, $1\frac{3}{4}$ or 2 inches. Further, no drill shall be used for boring a shot-hole unless it allows a clearance of at least $\frac{1}{8}$-inch over the diameter of the cartridge to be used.[1]

Statistics.

The following Table gives the quantities of different explosives that were used in Great Britain and Ireland in coal and metalliferous mines and in quarries under the Quarries Act in 1910:

	Quantity used lbs.	Percentage
Permitted Explosives	8,607,882	28·2
Gunpowder	17,664,483	57·8
Gelignite	3,039,256	10·0
Gelatine dynamite	494,560	1·6
Blasting gelatine	257,756	0·9
Blastine	165,456	0·5
Cheddite	123,584	0·4
Saxonite	118,886	0·4
Various	66,258	0·2
	30,538,121	100·0

[1] *Explosives in Coal-Mines Order*, May 21, 1912; *A.R.*, 1912, p. 32.

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In 1911 the quantities were :

	Quantity used lbs.	Percentage
Permitted explosives	9,340,033	30·0
Gunpowder	17,305,073	55·3
Gelignite	3,294,423	10·3
Gelatine dynamite	472,464	1·5
Blasting gelatine	244,155	0·8
Blastine	155,788	0·5
Saxonite	135,548	0·4
Cheddite	110,761	0·4
Polarite	88,491	0·3
Steelite	75,560	0·2
M.B. powder	51,950	0·2
Various	23,642	0·1
	31,297,888	100·0

Military blasting.

High explosives for military use have to satisfy somewhat different conditions to those employed for civil purposes. In order to be safe under the trying conditions of active service it is necessary that the explosive shall not be too sensitive to shock or friction. Secondly, demolitions must often be carried out in a minimum of time, so that it is not possible to make a boring to take the charge, which must be detonated freely exposed or only covered with a little earth. The explosive should therefore have a high velocity of detonation, high power and high density.

Gun-cotton.

For many years wet gun-cotton was used for this purpose, as it possesses all the qualities mentioned except that its density is rather low. It is so insensitive, however, that a primer of dry gun-cotton has to be used to detonate it, which complicates the operation somewhat, and in hot climates causes trouble on account of the limited life of dry gun-cotton.

For this purpose the gun-cotton is compressed in powerful hydraulic presses. The moulded blocks or cylinders (*see* p. 165) are placed in the press and subjected to a pressure of 4 to 7 tons per square inch, whereby the height is reduced to about a third, and the moisture to about 15 per cent. The density of the compressed gun-cotton is from 1·05 to 1·2. Occasionally part of the gun-cotton explodes whilst being subjected to pressure. The damage done does not usually extend beyond the press, but for the sake of safety the man who works the press should be protected by means of a rope mantlet or other suitable guard. The compressed gun-cotton is as hard as wood, and can be cut with ordinary wood-working tools provided it is kept thoroughly wet. Use is made of this fact to shape slabs to be used for charging submarine mines and torpedo war-heads, also to drill holes in the primers to take the detonators. The primers are afterwards dried by means of hot air until they only contain about 1 per cent. of water and are waterproofed.

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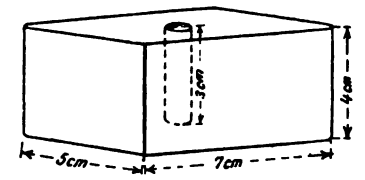
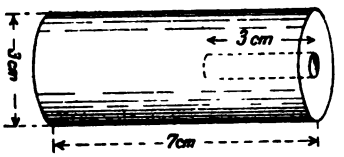
Many of the Powers use picric acid, which has a higher velocity of detonation and a higher density than compressed gun-cotton. Its power is slightly less weight for weight, but bulk for bulk it is greater. In Germany it is compressed to a density of 1·5 to 1·55, and under the name of Sprengmunition 88, is made up in the forms shown in Fig. 71. To protect them against moisture and crumbling, the outer layers of the "Sprengkörper" and "Bohrpatrone" are impregnated to a depth of about 4 mm. with paraffin, and are wrapped in paraffined paper, and the hole for the detonator is closed with a disc of paper. The Sprengkörper weighs about 200 g., and the Bohrpatrone 75 g. The "Sprengpatrone" consists of five Sprengkörper in a tin box with holes on three sides for detonators and wires to bind them on. Picric acid of this density can be detonated directly by means of a 1 g. detonator, but it is better to use a more powerful one. In France, under the name of Mélinite, picric acid is made up into cylindrical cartridges weighing 100 g., and oblong boxes holding 60 g. and 135 g. and 20 kg. respectively.

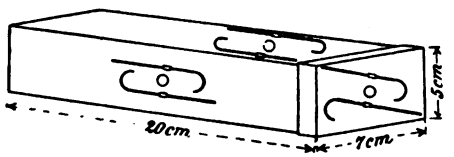
Picric acid.



Sprengkörper



Bohrpatrone



Sprengpatrone

Fig. 71. Dimensions of German Military Blasting Cartridges

Picric acid has two great disadvantages: it is liable to form highly sensitive picrates, if it comes in contact with basic substances, or metals other than tin or zinc, and if it is wet it loses its power of detonating. For these reasons there is a strong tendency to use trinitro-toluene instead of picric acid. The velocity of detonation, power and density of trinitro-toluene are all slightly lower, but not sufficiently so as to make much practical difference. In Germany, under the name of Sprengmunition 02, it is compressed to a density of 1·45 to 1·5 and made up into cartridges of the same dimensions as Sprengmunition 88. In Spain the same substance is used under the name of Trilit, and in France under that of Tolite: other fancy names are Trinol and Trotyl. Trinitro-toluene requires a more powerful detonator than picric acid: a 2 g. detonator is not always sufficient, and it is better to use one containing a small quantity of a more powerful explosive in addition to fulminate.

Trinitro-toluene.

There are other nitro-derivatives which have greater power and a higher

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velocity of detonation than trinitro-toluene, for example, tetranitro-methyl-aniline, but their high cost of manufacture prevents their use on a large scale. In the French army trinitro-cresol is used under the name of Cresylite, either by itself or mixed with picric acid. It has the same disadvantages as picric acid.

Smokeless powder.

Smokeless powder is also sometimes used for demolitions, but is difficult to detonate, especially the larger sizes, and has rather a low velocity of detonation: a powerful detonator is required. Ballistite is used largely in Italy for this purpose.

The ordinary commercial explosives are also used by military engineers.

Captain Zschokke of the Swiss army has given the following results of tests on various high explosives: [1]

	Power	Sensitiveness	Brisance
	Trauzl Test	Falling Weight Test	Crusher Test
	c.c.	cm.	Per cent.
Blasting gelatine	632	15	9·1
Gelatine dynamite (75 per cent. N/G)	517	15	14·7
Westfalite (Am. nitr. expl.)	442	55–60	12·0
Cheddite C (chlorate expl.)	378	20	21·0
Smokeless powder (N/c 82, T/n/t 18)	350	25	7·8
Picric acid, cast, sp. gr. 1·76	325	30	—
Gun-cotton, 2 per cent. water, sp. gr. 1·12	368	25	21·0
Guhr dynamite (70 per cent. N/G)	316	20	23·4
Trinitro-toluene, compressed, sp. gr. 1·50	300	80	31·8
Picric acid, compressed, sp. gr. 1·63	300	30	35·5
Cheddite 41	300	40	11·4
Cheddite 60 N.	288	18–20	16·7
Cheddite 60	273	15–20	15·5
Trinitro-toluene, cast, sp. gr. 1·61	260	80	—
Petroklastite	157	100	—
Blasting powder	108	65	—

For most of the tests 2 g. detonators were used containing a little trinitro-toluene; only for trinitro-toluene itself special ones were employed containing 2 g. of tetranitro-methylaniline. The falling weight tests were carried out with Lenz's apparatus with a 10 kg. weight falling on to a quantity of 0·15 to 0·2 g. (according to the density) pressed into a tablet 0·5 sq. cm. in area and 2·5 mm. high, wrapped in tin-foil. For the brisance test quantities of 10 g. were used. In the Trauzl tests on the last two explosives the charges were tamped with quick-setting cement. For further particulars concerning these various tests *see* Part VIII.

[1] *Militarische Sprengtechnik*, 1911.

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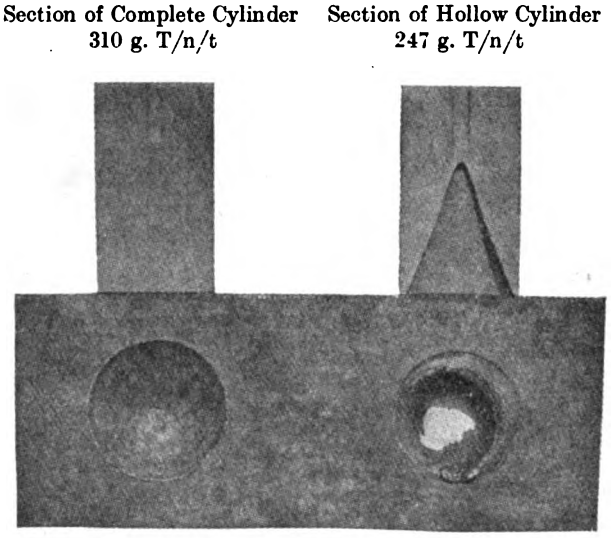
For demolitions carried out with unconfined charges it is important to remember that the action of the explosive is much more powerful in the direction in which the wave of detonation is travelling. The results obtained by Kast with the brisance-meter indicate that no useful purpose is served by increasing the length of the cartridges under these conditions to more than 75 mm. (3 inches).[1] It has been found by Neumann [2] that if a charge be hollowed out as shown in Fig. 72, the effect is intensified considerably. The reason seems to be, that when the wave of detonation reaches the cone-



Wrought iron plate 25 mm. thick on which both charges were detonated in upright position

FIG. 72. Effect of Hollowing-Out a Charge

shaped hollow, waves of compression start out perpendicularly to the conical surface, and these meet in the centre, producing a much greater effect than an ordinary detonation wave; just as there is an intensification of effect where two waves meet in a piece of detonating fuse.

Submarine mines.

For submarine mines and torpedo war-heads the requirements are much the same as for military blasting explosives. As long ago as the Crimean War (1854–1856), Emmanuel Nobel is said to have used mines of gun-cotton to protect the mouth of the Neva. Picric acid has been used, but now the tendency is to employ trinitro-toluene. Nitro-glycerine explosives are not suitable on account of their low stability.

[1] *See* chap. xxviii.

[2] *Ang.*, 1911, p. 2238. Also *S S.*, 1914, p. 183.

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Shell. As a filling for shell, black powder was used almost exclusively until a comparatively late date, as its insensitiveness to mechanical influences enables it to withstand the shock of discharge with safety, and even if it explodes in **Shrapnel.** the gun it does not do any serious damage. It is still used for Shrapnel, as it possesses ample power to drive the bullets out of the shell casing, and the smoke it produces is an advantage, in that it enables the artillerymen to see where the shell burst. Endeavours are in fact being made to increase the amount of smoke.

Common. Soon after the discovery of gun-cotton attempts were made to use it for filling shell, especially in Austria, but it has never met with much favour for this purpose. Wet gun-cotton is very difficult to detonate, and if there be a priming of dry gun-cotton there is danger of premature explosions. Nitroglycerine explosives have not been much more successful. Austria has tried blasting gelatine "phlegmatized" with camphor, but even so it must be dangerously sensitive; moreover, even without the addition of camphor it is not easy to obtain the maximum velocity of detonation, and the stability falls off rapidly on keeping. Italy is said to have used Ballistite, to which the same objections may be raised, except that it is not mechanically sensitive. The first satisfactory solution of the problem was the adoption of picric acid by France. This was quickly followed by similar measures taken by practically all the other Powers, each of whom, however, gave the substance a different name:

France	Mélinite
England	Lyddite
Germany	Granatfüllung 88
Italy	Pertite
Japan	Shimosite
Sweden	Coronite
Spain	Picrinite
Austria	Ecrasite

In Mélinite there is sometimes an addition of trinitro-cresol (crésylite), which reduces the temperature of fusion, and so facilitates the pouring of the molten material into the shell, and at the same time does not seriously affect the explosive properties. Ecrasite, too, is said sometimes to contain the same addition, or to be composed of the ammonium salt of trinitro-cresol.

Picric acid is now being replaced everywhere with trinitro-toluene for the same reasons that have caused the latter to be used for demolitions, and also because its melting-point is much lower. When picric acid is detonated, a part of the carbon separates as such, producing black smoke, and trinitro-toluene gives rise to a larger proportion. This involves a considerable diminution in the volume of gas formed, and also in the heat evolved, and consequently the power is not so great as if all the carbon and hydrogen were oxidized.

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The most suitable oxidizer to add to make up the deficiency of oxygen is a nitrate, and of the nitrates that is best which contains most available oxygen in unit space; for space in this case is of more importance than weight; it is also desirable that the substance used should not be deliquescent. The following are the properties of the nitrates that might be considered:

	Specific Gravity	Available Oxygen		Relative Deliquescence 17° C.
		per gramme	per c.c.	
Sodium nitrate	2·26	0·47	1·06	4·3
Potassium nitrate	2·08	0·40	0·82	1
Barium nitrate	3·2	0·31	0·98	0·23
Lead nitrate	4·58	0·24	1·12	0·7

Lead nitrate is therefore the best: over sodium nitrate it has the advantage not only that it is not deliquescent, but also that its oxide has not the same tendency to take up carbon dioxide and so diminish the volume of gas formed on detonation. Macarite is a mixture of trinitro-toluene with sufficient lead nitrate for complete oxidation. The velocity of detonation is somewhat less than that of the trinitro-toluene alone, but this is more than counter-balanced by the increase in the power, with the result that the brisance is higher. The objection has been raised, however, that lead nitrate mixtures are rather sensitive.

In order to prevent premature detonations in the gun special care has to be exercised in the design and manufacture of the shell and the fuse. The Japanese had several severe accidents of this kind during their war with Russia. Other additions have been made to trinitro-toluene to diminish its sensitiveness: Plastrotyl contains a small proportion of resin, and Triplastite consists of a mixture of trinitro-toluene and lead nitrate made plastic by means of liquid dinitro-toluene gelatinized with collodion cotton.

Armour piercing shell.

For the attack of war-ships, shell are required that will pass through the armour and explode when they are on the other side. By providing the shell with a cap of soft iron to protect its nose, and by suitable construction, the mechanical difficulties of obtaining a projectile which can perform this feat without breaking up, have been overcome to a great extent. A high explosive is now wanted, that will not be exploded by the tremendous shock caused by the impact of the shell on the armour at a velocity of several thousand feet per second. Black powder will accomplish this, and armour-piercing shell are still often filled with it: the nitro-aromatic explosives, on the other hand, generally detonate on the face of the armour-plate. Ammonium nitrate explosives, and especially Ammonal, are said to satisfy the requirements,

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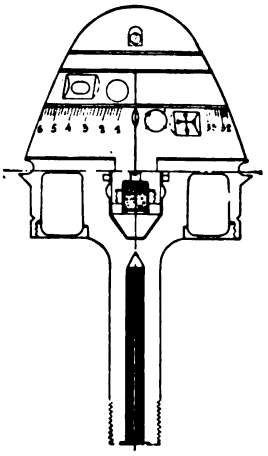
but they have the disadvantage of being extremely deliquescent, which makes their storage for long periods difficult. Moreover, their velocity of detonation is comparatively low.



For all shell except shrapnel high brisance is desired; it is not sufficient merely to burst the shell: it should be broken into as many effective missiles as possible, to be projected around with a high velocity.

High-explosive shrapnel.

Now that field-guns are provided with steel shields, shrapnel bullets are no longer effective against them. For this reason, amongst others, the artillery of most of the Powers have been provided with high explosive shell in addition to shrapnel. But this complicates the equipment, especially as the two descriptions of shell do not range equally. Hence the tendency now is to have a universal shell, which will serve both purposes; that is to say, a shrapnel shell containing a charge of high explosive, as well as the charge of gunpowder for the expulsion of the bullets. Various methods have been proposed for carrying this out. In some the high explosive charge is in the head. After the gunpowder has been exploded by the time fuse, and the bullets have been ejected, the head travels on by itself, and when it strikes an object it is detonated by the impact portion of the fuse, or if it reaches its billet before the time fuse has functioned, the impact fuse acts and scatters all the contents of the shell. In others the bullets are embedded in melted trinitro-toluene instead of in resin or sulphur. Space is thus saved.

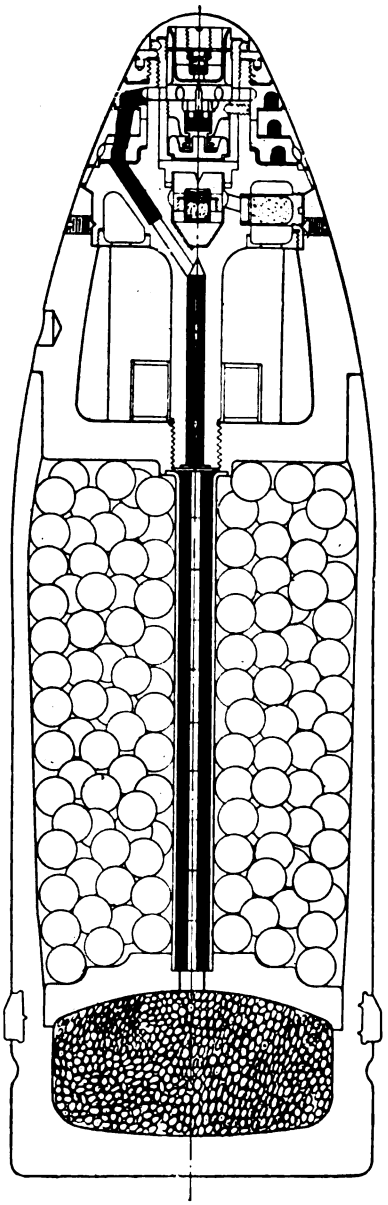


FIG. 73. Ehrhardt Universal Shell 4·2″ Howitzer

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When the powder charge explodes it scatters the bullets and the trinitrotoluene, which is partly burnt, but does not detonate. But there is also a fuse, which will cause the detonation of the high explosive. The fuses of these shell are necessarily somewhat complicated, but advantage is generally taken of the fact that the shrapnel part is mostly required to act with a time fuse, and the high explosive on impact. Some designs, however, provide also for the shrapnel to act on impact if desired, or the high explosive after a fixed time. For further information concerning these high explosive shrapnel shell *see* a paper by Colonel Bethel in the *Jour. Roy. Art.*, 38, p. 371.

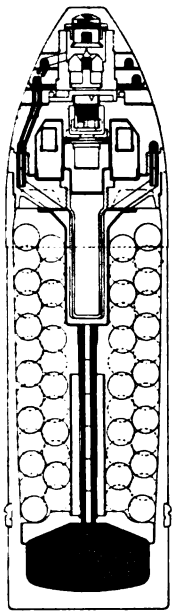

FIG. 74. Krupp Universal Shell with Quadruple Action Fuse

In the Balkan War it was found that the heads of the universal shell were very liable to burst in the air when the shrapnel charge of gunpowder was set off by the time fuse. The makers are now adding a small burster between the bullets and the head to blow the head off before the main burster has time to act.[1]

Grenades.

The hand-grenade, which was introduced in the seventeenth century, and was very largely used during the wars of the eighteenth, lost its importance in the time of the Napoleonic wars, but its use did not cease entirely, for it was employed in 1808–1809 at Saragossa, in 1832 at Antwerp, in 1854–1856 at Sebastopol, and in 1884–1886 by the English in the Sudan. During the Russo-Japanese War (1904–1905) the hand-grenade regained much of its old importance, and the principal Powers are now providing them as a regular part of their equipment. From the point of view of explosives they present no special interest; the difficulties to be overcome are mechanical. A grenade weighing about a pound can be thrown by hand approximately 50 yards, and its radius of action is about 20 yards, consequently the weight cannot be made much more than this without danger to the thrower. The fuse should either act only on impact, or if it be a time fuse should be so arranged that it only becomes active after it has been thrown. Whilst practising with a primitive grenade in which these precautions had not been taken a British officer was killed at Rurki, in India, in September 1911. Grenades are also made to throw with a sling, and there are rifle-grenades, such as that of Hale, which can be propelled from a rifle a few hundred yards.[2] This has a rod, which goes down the barrel of a rifle, and it is fired by an ordinary small-arm cartridge, from which the bullet has been extracted. For further information concerning grenades *see* Andersch,

[1] Private communication from Colonel Bethel.

[2] Eng. Pat. 4925 of 1911.

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S.S., 1913, pp. 22, 48 and 68. The explosives most used for grenades are picric acid, trinitro-toluene, compressed gun-cotton, tonite, and smokeless powder.

Flying machines.

In the case of bombs to throw from flying machines there is not the same limitation as to weight. The principal difficulty here is to attain a sufficient precision without approaching the enemy so close as to place the aviators in great danger. Some ingenious appliances have been designed for dropping explosives with accuracy, but it remains for the future to show whether, to their undoubted value for scouting, the flying machines will be able to add real effectiveness as engines of assault.

For the attack of flying machines special guns are now made for very high angle fire. For the destruction of dirigibles endeavours are directed to setting fire to the hydrogen in the balloons, but this is not so easy as it seems, because the projectile passes through the envelope so rapidly that it has no time to ignite the gas in the ordinary way.

Tracers.

In order to get the range of such a rapidly moving object as an aeroplane or a torpedo boat it is found desirable to render the course of the projectiles visible. For this purpose Semple has devised "tracers," which are fitted to the base of the shell. For use by day the tracer is filled with a dark coloured liquid, which is ejected during flight as a fine spray. The night tracers are filled with a fire-work mixture, which is ignited by the propulsive charge, and renders the course of the projectile visible like that of a rocket.

Products from Explosives

Carbon monoxide.

Some of the products formed by explosives are poisonous, notably carbon monoxide, which is produced in considerable proportion whenever the oxygen in the explosive is insufficient to convert all the carbon into dioxide and the hydrogen into water. The gases from black powder of standard composition contain from 8 to 17 per cent. of carbon monoxide by volume, but if the percentage of saltpetre be less than 75, of course there is more. Blasting gelatine contains just about enough oxygen for complete combustion, whereas British gelatine dynamites and gelignites usually have a slight excess. Ammonium nitrate explosives often contain a considerable excess of oxygen, but they vary very much in this respect, and some are deficient in this constituent. Many of the explosives used in coal-mines give more carbon monoxide than dioxide. As a rule the ventilation is so good that no evil consequences result, but this is not always the case. In the days when black powder only was used, mine sickness was a frequent complaint and was due to poisoning with carbon monoxide. In 1904 in a mine at Grängesberg two miners were found dead, presumably from this cause,[1] and in 1908, when an underground maga-

[1] Nauckhoff, *S.S.*, 1909, p. 241.

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zine exploded in a coal-mine in West-Essen, five men were fatally poisoned by the gas formed, in addition to six killed directly by the explosion. In the South African gold-mines the miners suffer much from what is generally called "miners' phthisis," and in 1902–1903 a Royal Commission inquired into the matter and found that it was due principally to carbon monoxide, which was found to be present in mine air. The explosives used contain sufficient oxygen for their complete oxidation, but it has been shown by Weiskopf [1] that the formation of the monoxide is due to the paper in which the cartridges are wrapped.[2] Mann carried out numerous experiments in the gold-mines of Western Australia,[3] and in samples of air taken as soon as possible after firing the charges he always found carbon monoxide, and in some cases, where a number of holes were fired simultaneously, there was over 1 per cent. In the trials with blasting gelatine, gelatine dynamite and gelignite, from a seventh to a seventeenth of the carbon appeared as monoxide, the mean being a twelfth. When the diameter of the cartridges was increased there was less carbon monoxide, and when the wrappers were removed the proportion was reduced to about a fiftieth. Similar results have been obtained by C. Hall and S. P. Howell with American explosives.[4] Increasing the proportion of oxygen in the explosives was not very effective, neither was the use of special "anti-fume" composition; and as it is not desirable to remove the wrappers in ordinary work, the only really satisfactory way to prevent injury to the miners is to have very good ventilation, and to prevent them approaching the working face until the fumes have had time to dissipate. The safety fuse also produces a considerable amount of carbon monoxide, but this source of trouble may be avoided by the use of electric detonators. If the material that is blasted be of a reducing character, such as coal or sulphide ore, it is inevitable that much monoxide will be produced, whatever measures be taken. Heise states [5] that between 1895 and 1898 there were ten fatal cases of poisoning with carbon monoxide in German coal-mines, although the dynamite used always contained an excess of oxygen.

The highly poisonous character of carbon monoxide is due to the fact that its affinity for the hæmoglobin of the blood is about 250 times that of oxygen. Consequently, when a man works in an atmosphere contaminated with the gas, his blood gradually becomes more and more inactive, and it only regains its full power of supporting life many hours after the man has returned to a normal atmosphere. If the amount of the gas exceed 0·02 per cent., symptoms of poisoning will appear when a man has been working for some hours. Up to 0·05 to 0·1 per cent. a man can bear it without serious

[1] *J. Chem. Met. and Min. Soc. of S. Africa*, 1909, p. 258; *S.S.*, 1909, p. 352.
[2] *See also* Moir, *J. Chem. Met. and Min. Soc. of S. Africa*, vol. iv., p. 46.
[3] *Report to W.A. Parliament*, 1911.
[4] *Bull.* 48, 1913, p. 16.
[5] *Glückauf*, 1899, p. 341.

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inconvenience for a half to one hour, whereas in the same space of time 0·2 to 0·3 per cent. is dangerous to life. It can be detected in air by the decolorizing effect it has on palladium chloride solution : as little as 0·04 can be detected with certainty by this method.[1] Its poisonous action on small birds, such as canaries, can also be utilized : 0·25 per cent. affects a bird in one minute, and in three minutes makes it fall from its perch.[2] It is best estimated by the quantity of iodine set free from heated iodine pentoxide.[3] For the cure of cases of poisoning of this kind, inhalation of oxygen is the only effective measure.

The high explosives mostly used for military demolitions, gun-cotton, picric acid and trinitro-toluene, form large quantities of carbon monoxide when detonated. Hence they are very unsuitable for use in underground workings.

Nitrogen oxides.

When properly detonated practically all the nitrogen in ordinary explosives is liberated in the elementary state, but those that contain a large excess of oxidizable substances generally give some ammonia as well. Very little oxide of nitrogen is formed even by highly oxidized explosives : Mann estimated that in the air immediately after firing shots there was on an average 0·0047 per cent. NO_2 ; the greatest quantity he found was 0·025 per cent. These quantities are of minor importance compared with those of the carbon monoxide. But when explosives burn, most of the nitrogen is liberated as nitric oxide NO, and this is converted by the air into the peroxide NO_2, and the same occurs to a great extent in the case of a blown out shot. Hence with these there is danger of poisoning with nitrous fumes. A blown-out shot should therefore never be approached too soon. The smell of the nitrous fumes is always perceptible, but the danger of the nitric peroxide lies in the fact that its full effects appear only some hours after inhalation. There are many cases on record of men going home apparently quite recovered from the effects, and then dying in convulsions in the night. As a cure doses of chloroform water were formerly much recommended,[4] but Curschmann after investigating the matter, came to the conclusion that chloroform is no good, and may be injurious. Inhalation of oxygen he considers to be the only effective measure.[5]

Acrolein, prussic acid, nitro-glycerine.

Blown-out shots are liable to produce other poisonous gases and vapours, such as acrolein and prussic acid. Nitro-glycerine explosives distil off part of this constituent, which condenses again to a fine mist in the air : if a sweet taste be observed in the air, the miner should leave at once and not return until it has disappeared.[6]

Hydrochloric acid.

Ammonium perchlorate explosives, such as Blastine, form hydrochloric

[1] *See* Nauckhoff, *S.S.*, 1909, p. 241.
[2] Burrell, *Bureau of Mines Technical Paper* 11.
[3] *See* Weiskopf, *loc. cit.*
[4] *A.R.*, 1904, App. V.
[5] *Deutsche Medizinische Wochenschrift*, 1911, No. 22 ; *S.S.*, 1911, p. 418. But *see also P. et S.*, vol. xvi., p. 200.
[6] *See* Jakobj and His, *S.S.*, 1907, p. 261.

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acid. This is about ten times as poisonous as carbon monoxide, but probably is not so dangerous as its presence cannot escape notice.

Black gunpowder and other explosives containing sulphur yield a considerable proportion of hydrogen sulphide (sulphuretted hydrogen) when they explode. This unpleasant and poisonous gas is therefore amongst the products of many American dynamites. The following Table shows the products obtained when various American explosives were fired in a Bichel pressure gauge. A charge of 200 g. in its original wrapper was used in each test, except with black blasting powder of which 300 g. were used. **Hydrogen sulphide.**

COMBUSTION PRODUCTS RESULTING FROM TESTS OF EXPLOSIVES IN THIN PARAFFINED PAPER WRAPPERS

(A. L. Hyde, analyst, *Bull.* 48, p. 10)

Class and grade of explosive	No. Electric detonator used.	Weight of products of combustion (grammes)			Gaseous products (per cent. by volume)							Solids (per cent.)		Volume of gas (litres)
		Gaseous	Solid	Liquid	Carbon dioxide	Carbon monoxide	Oxygen	Hydrogen	Methane	Nitrogen	Hydrogen sulphide	Soluble	Insoluble	
30 per cent. "straight" nitro-glycerine dynamite .	6	96·8	102·1	12·9	22·9	28·4	0·0	20·6	0·7	27·4	—	88·00	12·00	85·8
40 per cent. "straight" nitro-glycerine dynamite .	6	107·4	87·1	12·4	27·3	26·9	·0	18·0	·4	27·4	—	86·73	13·27	88·5
50 per cent. "straight" nitro-glycerine dynamite .	6	124·6	70·3	14·7	24·4	31·2	·0	20·7	·7	23·0	—	79·14	20·86	105·5
60 per cent. "straight" nitro-glycerine dynamite .	6	143·5	49·6	11·9	22·2	34·6	·0	23·2	·8	19·2	—	68·53	31·47	128·9
60 per cent. strength low-freezing dynamite . .	6	161·5	43·5	3·9	8·9	47·4	·0	31·0	·6	12·1	—	78·76	21·24	169·5
40 per cent. strength ammonia dynamite . . .	6	95·7	85·9	26·1	41·4	3·8	·0	3·1	·8	45·5	5·4	86·03	13·97	65·6
40 per cent. strength gelatine dynamite . . .	6	96·3	96·3	11·7	50·8	3·0	·0	1·8	·8	39·5	4·1	87·32	12·68	60·3
5 per cent. granulated nitro-glycerine powder [2] . .	6	115·5	93·6	8·3	51·3	2·7	·0	·9	·7	28·7	15·7	78·00	22·00	61·6
FFF black blasting powder	([3])	154·4	126·9	4·1	49·7	10·8	·0	1·8	·6	28·4	8·7	91·20	8·80	67·8

[1] The explosives named in this Table are not of the same formulas as those in the Tables on pp. 282, 283, 289.

[2] Primer of 40 per cent. "straight" nitro-glycerine dynamite, representing 10 per cent. by weight of the charge, was used, but the gases evolved by the dynamite were deducted in the computations of the volume of gas (litres).

[3] Black-powder igniter used.

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PART VIII

PROPERTIES OF EXPLOSIVES

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CHAPTER XXVI

PHYSICAL CHARACTERS AND TESTS

External examination : Colour : Density : Flashing test : Shaking test : Absorption of moisture : Deliquescence : Exudation : Test for liquefaction : Wrappers : Pressure test : Keeping test : Centrifugal test : Sensitiveness and danger in handling : Friction test : Falling weight test : Sensitiveness to detonation : Effect of temperature : Transmission of detonation : Sensitiveness to heat : Temperature of ignition : Tests of International Committee

External Examination

The external examination of an explosive comprises the observation of its general appearance and character. In the case of black powders the lustre, hardness, shape and size of the grains are all matters of importance. The size of the grains is determined by sifting a known weight through a series of sieves and ascertaining what proportions pass through the different meshes.

At the American Bureau of Mines the following characteristics of blasting explosives are noted :

1. Granulation. Structure : (*a*) granular, (*b*) fibrous, (*c*) powdered. Size : (*a*) very fine, (*b*) fine, (*c*) coarse, (*d*) very coarse.
2. Liquidness : (*a*) very wet, (*b*) wet, (*c*) dry, (*d*) very dry.
3. Hardness : (*a*) very hard, (*b*) hard, (*c*) soft, (*d*) very soft.
4. Cohesiveness : (*a*) very cohesive, (*b*) moderately cohesive, (*c*) slightly cohesive, (*d*) not cohesive.

Colour.

According to Benjamin [1] the colour may be measured by means of a Maxwell rotating disc. A circular brass plate 29 cm. in diameter is mounted so that it can be rotated, and on it are placed the various colour discs, which have a diameter of 25 cm., and are held in place by means of a cover of celluloid. The colour discs are adjusted until on rotating the apparatus the colour exactly matches that of the explosive. The amount of the various constituents is then read off on a scale round the circumference of the brass disc, and the figures thus obtained serve to define the colour.

Density

Absolute specific gravity.

The absolute specific gravity of an explosive may be ascertained by reducing it to a very fine state of division, introducing a known weight into a specific

[1] *Eighth Int. Cong.*, vol. iv. p. 12.

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gravity bottle, filling up with a liquid that has no action on the powder, removing all air under a vacuum pump, and weighing after bringing it to standard temperature in the usual way for the determination of the specific gravity of solids. This, however, is a determination that is seldom carried out, as the absolute specific gravity does not often require to be known for practical purposes, and it can be calculated with sufficient accuracy from the known specific gravities of the different constituents.

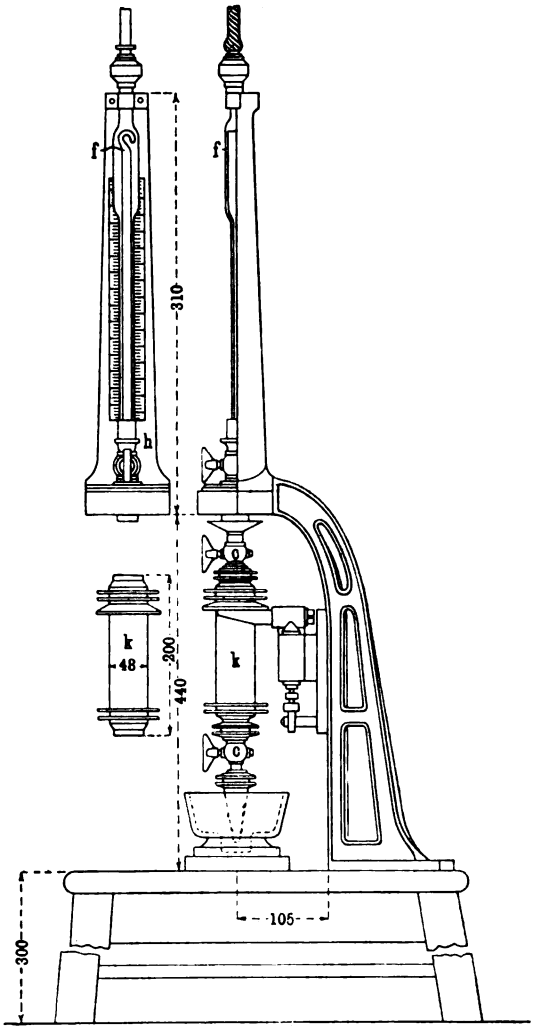

Fig. 75. Bianchi's Densimeter

Density.

By the density of an explosive is usually meant the density of the individual pieces or grains including any air there may be in the pores or interstices. It is determined by ascertaining the volume of some suitable medium that is displaced by a known weight of the explosive. This volume depends to some extent on how far the medium is caused to penetrate into the pores of the material. For black powder Bianchi's apparatus is generally used (Fig. 75), and the medium is mercury. It consists of a vessel, *k*, which can be screwed on to the apparatus so that the whole constitutes a sort of barometer. Two steel cocks screw on to *k*: the lower one has a tube drawn out to a point which dips into a basin of mercury, the upper one screws on to an upright tube, *f*, which has graduations. At either end of *k* there is a piece of fine iron wire gauze to prevent grains of powder escaping. One hundred grains of powder are weighed out into *k*, which is then connected up, and the air is pumped out through the top of *f* by means of a vacuum pump, until the mercury attains a steady level. The lower cock is then closed, the vacuum is broken so that the powder is under a certain head of mercury, then the upper cock is closed and *k* is disconnected and weighed. The mercury is

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then run out and the operations are repeated; the weight should then be the same. The mercury should be brought to a standard temperature before the determination and maintained at it. If S be the specific gravity of mercury at this temperature, and W the weight of the vessel filled with mercury alone, and W^1 the weight filled with powder and mercury, then the density of the powder is equal to

$$\frac{S \times 100}{(W - W^1) + 100}.$$

If the powder be of larger size than RLG² it is first broken up in a mortar and the dust is sifted out and discarded.

For moulded prismatic powders use is made of Bode's densimeter, in which the volume is ascertained by finding the weight required to immerse a prism below the surface of mercury. The calculation is much the same as with Bianchi's apparatus.

At the 8th International Congress Snelling described a densimeter (Fig. 76), which works somewhat on the same principle as the Bianchi, but does not require a vacuum pump, a Torricellian vacuum being formed by forcing mercury from the vessel e into a by means of water pressure, and then opening the waste cock x, so that

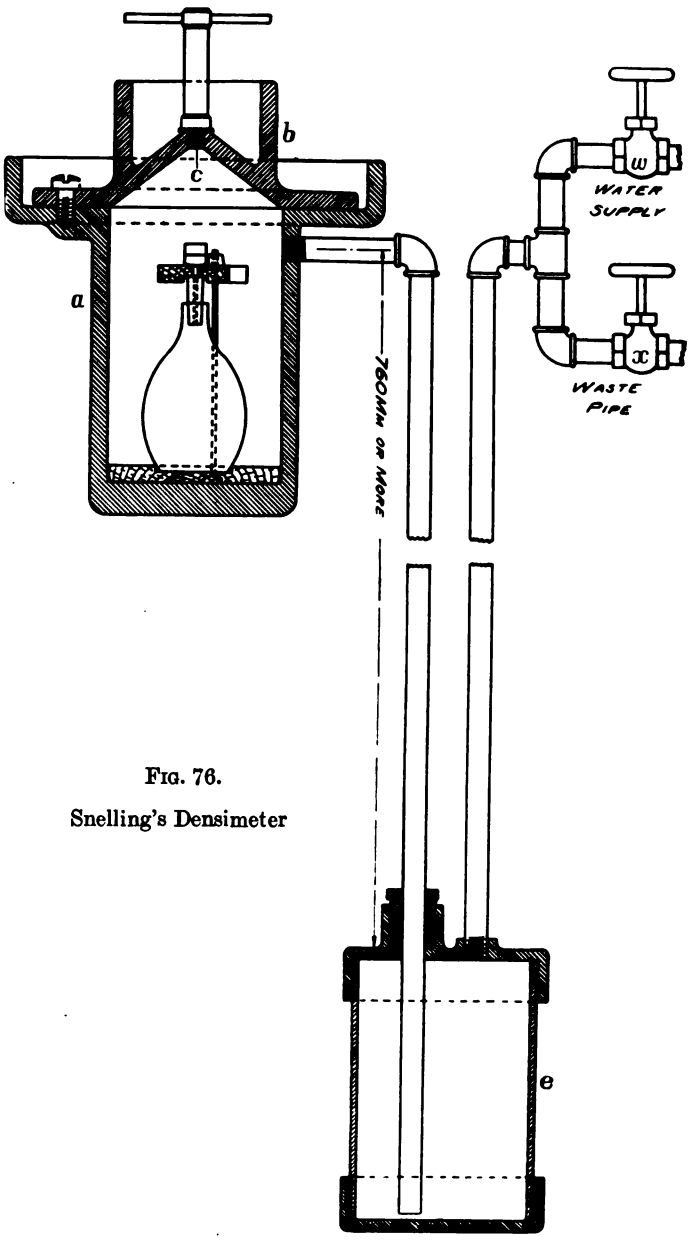

FIG. 76.

Snelling's Densimeter

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the pressure is relieved. The powder is weighed out into the pyknometer, which is clamped down inside *a*, and the lid *b* screwed on. The cock *w* is opened, so as to force the mercury into *a*, and the valve *c* is opened to allow the air to escape. When mercury commences to come through *c*, *c* and *w* are closed and *x* is opened, whereby a vacuum is formed in *a*. Then *x* is closed and *w* opened and the whole cycle of operations is repeated until no more air is removed through *c*. Then the pyknometer is taken out and weighed.

The densities of black powders found by these methods are usually within the limits 1·65 to 1·85, but the absolute specific gravity as calculated from those of its constituents is considerably higher; that of saltpetre is 2·08, of sulphur (rhombic) 2·05; that of charcoal depends upon the burning process and is difficult to determine on account of the pores, but it is at least 1·5 and may approach that of graphite 2·2. The absolute specific gravity of black powder is therefore at least 2·03, which shows that under the conditions of the density determinations, many pores in the interior of the grains do not become filled with mercury.

The density of high explosives may be ascertained by carefully measuring and weighing a cartridge, but in consequence of the irregular shape, this may not give a satisfactory result. The American Bureau of Mines determines it by weighing in sand. American 40 per cent. dynamite was thus found to have a density of 1·22 to 1·24. In Snelling's densimeter it gives results in the neighbourhood of 1·6, more nearly approaching the absolute specific gravity. The densities or "apparent specific gravities" of American safety explosives determined in sand varied from 0·84 to 1·54, those of European safety explosives from 0·68 to 1·36.

Gravimetric density.

The gravimetric density of a charge in a fire-arm is the weight of the charge divided by the weight of water that would be required to fill the chamber space. As applied to gunpowders it is the weight that will fill unit volume of a vessel when simply poured in and very gently shaken down. In Belgium vessels of 1, 2 or 10 litres capacity are used according to the size of the grains.[1] Above the vessel is fixed a funnel of somewhat greater capacity closed below by a slide. After the funnel has been filled the slide is removed and the powder allowed to run into the vessel. By means of a straight-edge it is then struck off level with the rim and weighed. The following are the densities of some German naval powders:

	Density	Gravimetric Density
Rifle powder M/71 . . . . . not under	1·655	0·915
New rifle powder M/71 . . . . . ,, ,,	1·755	0·945
Cannon powder	1·60	0·925
Large grain powder	1·66	0·970
,, ,, blasting powder	1·75	0·975

[1] Gody, *Les Explosifs*, p. 146.

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The difference between the gravimetric density and the ordinary density shows that there is almost as much free air space between the grains as is occupied by the grains themselves. Powders containing grains varying very much in size have higher gravimetric densities than those which are fairly uniform. Thus Snelling found a number of American blasting powders to have gravimetric densities from 1·09 to 1·20. There is no necessary connection between the ordinary and gravimetric densities.

Flashing Test

To ascertain whether they have been thoroughly incorporated black powders are submitted to the " flashing " test by burning them on a glass, porcelain or copper plate. The *Treatise on Service Explosives* gives the following instructions for carrying out the test : The powder is put into a small copper cylinder like a large thimble, which is then inverted on the flashing plate. This ensures that the grains of powder are arranged in much the same way each time, which is very important. If the powder has been thoroughly incorporated, it will " flash " or puff off when touched with a hot iron with but few " lights " or sparks, and leaving only some smoke marks on the plate. A badly incorporated powder will give many sparks, and also leave specks of undecomposed saltpetre and sulphur forming a dirty residue. Although a very badly worked powder can be detected at once, it requires an experienced eye to form an accurate judgment of the comparative merits of ordinary powders ; for if made from slack burnt charcoal, the powder will never flash so well as if the charcoal has been made at a high temperature. Powder, which has once been injured by damp will flash very badly, no matter how carefully it has been incorporated. This is because the saltpetre has passed partially into solution and segregated into crystals of comparatively large size.

Shaking Test

The shaking test is applied to an explosive to ascertain whether it has been so incorporated that the constituents will not separate out under the ordinary conditions of transit and use. The German Railway Commission places 100 g. in a dry wide-mouthed bottle of 150 c.c. capacity, which is shaken backwards and forwards horizontally 150 times a minute for five hours.

A test which more nearly imitates the conditions of actual transit consists in jerking it up and down vertically. The powder is placed in a closed copper canister, which is fixed to the steel table of the shaking machine. This is raised a few mm. by means of a cam and then falls with a jerk on to an adjustable steel stop. The apparatus can be provided with a counting arrangement, so that the number of falls is known. The separation of the ingredients, or other change in the explosive, may be seen in some cases by superficial examina-

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tion, in other cases it may be necessary to apply tests for sensitiveness or other physical properties, or to make chemical analyses of portions from the top and bottom of the small canister.

Absorption of Moisture

Amorphous materials, such as charcoal, wood-meal, flour and nitro-cellulose take up moisture from the air in amounts depending upon the temperature and the degree of saturation of the atmosphere. Crystalline substances behave quite differently in this respect: if the pressure of water vapour be below a certain amount, varying with the different substances and with the temperature, no moisture is taken up. At a higher pressure of water vapour a compound with a fixed number of molecules of water may be formed; and when the pressure of water vapour in the air is higher than the vapour pressure of a saturated solution of the substance it deliquesces, gradually becoming entirely liquid.

Hygrometric test.

In the case of black powder it is important that it should not absorb moisture rapidly in a moist atmosphere, and so be rendered unserviceable. Powders are therefore submitted to the "hygrometric test": 200 grains (13 g.) are put into a little tray with a bottom of fine wire gauze, and placed inside a box containing a considerable quantity of a saturated solution of saltpetre. Powders of the smaller sizes are allowed to remain in the box twenty-four hours, the larger sizes forty-eight hours. The powder is then weighed again, and the percentage gain in weight together with the moisture originally present in the powder is the hygroscopicity. If the special apparatus here mentioned is not available the determination can be made in an ordinary desiccator containing a saturated solution of saltpetre mixed with crystals of the salt, and 2 to 5 g. can be weighed out on to a watch glass. The results will be much the same.

Gunpowder made with charcoal carbonized at a low temperature absorbs moisture far more readily than that made with hard-burnt charcoal, but the absorption also depends very much on the purity of the saltpetre used for making the powder. If the saltpetre were absolutely pure, there would be practically no tendency for it to take up moisture from the saturated solution in the hygrometric box, but if there be a small proportion of a soluble impurity such as sodium chloride, there is tendency for a thin film of a solution saturated both with sodium chloride and potassium nitrate to be formed on the surface of each crystal. Such a solution has a much lower vapour pressure than that of a solution saturated with potassium nitrate only. Consequently, a very small proportion of sodium chloride will cause a great increase in the amount of moisture absorbed by the powder. Other soluble salts, such as sodium nitrate, have a similarly injurious effect. Even if a less soluble substance be mixed with the saltpetre, it will have a deleterious effect, because the solubility

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of two substances combined is nearly always greater than that of one alone. If the powder absorb sufficient water to make it moist, the grains will cake together, but a more serious effect is that the minute particles of ground saltpetre gradually coalesce into crystals of comparatively large size, and consequently even if the powder be dried again it will not regain its explosibility in full measure, unless it be worked again in a mill.

Deliquescence.

The following Table shows the tendency of pure potassium nitrate to absorb moisture at different temperatures :

Temperature	Solubility	Relative Humidity
0°	13·3	97·0
10°	20·9	96·5
20°	31·6	94·7
25°	37·3	93·8
30°	45·8	92·5
40°	63·9	90·0

In the middle column is given the number of parts by weight dissolved by 100 parts of water, and in the last column the amount of moisture in air in equilibrium with the saturated solution, the quantity of water vapour in air saturated with moisture from distilled water at the same temperature being taken as 100.

Blasting explosives frequently contain salts, such as the nitrates of sodium and ammonium, which are far more liable to deliquesce than potassium nitrate. It is useful to be able to express this property by a figure, and for this purpose the reduction of the vapour pressure of the saturated solution as compared with distilled water may be used, and in order to get a comparative figure, this may be divided by the corresponding reduction in the case of saltpetre at the same temperature. Unfortunately the vapour pressures of the saturated solutions at ordinary temperatures have been determined in practically no cases ; but those of solutions of various strengths have been measured at different temperatures in the case of most of the more important substances, and from these measurements the reduction of the vapour pressure in the case of the saturated solutions can be calculated, the solubilities being known. In the case of some organic substances, such as sugar, the reduction of the vapour pressure follows approximately Raoult's law, that is to say, the reduction of the vapour pressure is to the vapour pressure of pure water as the number of molecules of solute is to the sum of the numbers of molecules of solute and solvent. But inorganic salts, as a rule, reduce the vapour pressure by amounts considerably greater than those corresponding to Raoult's law. This is due partly to electrolytic dissociation, and partly to combination of the solute with the water. A factor can be obtained by which the figures corresponding to Raoult's law must be multiplied in order to obtain results giving approximately the reductions of vapour pressure caused by saturating water with the substances.

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In the Table on page 341, where the factors are in brackets, there have been no data from which to calculate them, and they have been estimated from analogy with other similar substances. In many cases the figures are only very rough approximations, but for ordinary purposes they are near enough. Moreover, the deliquescence is affected so greatly by the presence of traces of impurities, that highly accurate estimations would not enable one to predict the behaviour when exposed to moist air with much greater accuracy. When an explosive contains two or more soluble substances mixed together, it is likely to be more deliquescent than if it only contained one of them. In the column of "relative humidity" is given the amount of moisture in air which is in equilibrium with the saturated solution, air saturated with water vapour being taken as 100. If the humidity of the air be less than this the pure substance will not deliquesce; if greater it will. This number subtracted from 100 and divided by the corresponding value for potassium nitrate gives the "relative deliquescence."

Any substance, which has a relative deliquescence above 3, requires to be stored under such conditions that moist air cannot obtain access to it. The cartridges of explosives containing nitrate of sodium or ammonium are therefore generally dipped into paraffin wax. As the ammonium salt is about twice as hygroscopic as the sodium compound, this precaution is specially necessary with the important class of explosives containing it. The French "Commission des Substances explosives" carried out experiments in which these salts, and mixtures of them, were exposed to atmospheres containing various amounts of water vapour:[1] the results are in accordance with the figures given in the table.

Explosives containing ammonium oxalate are no longer required in England to be enclosed in waterproofed inner packages.[2] This also is in accordance with the above calculations, which show that ammonium oxalate is one of the least deliquescent of the substances that are used in the manufacture of explosives; the danger is rather that efflorescence may occur.

Exudation

Explosives containing nitro-glycerine are liable under certain circumstances to sweat out some of this substance, and this is a source of serious danger. Kieselguhr dynamite, for instance, gives up practically the whole of its nitro-glycerine if it becomes wet. If the guhr is over or under calcined, or if it be insufficiently absorbent, this tendency is much increased.

Gelatinized explosives are liable to become too liquid at a moderately high temperature, if the collodion cotton be of an unsuitable character, or if

[1] *P. et S.*, vol. xvi, 1912, p. 9.

[2] *A.R.*, 1910, p. 43.

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Substance	Formula	Molecular Weight	Solubility	Temperature	Factor	Relative Humidity	Relative Deliquescence $KNO_3 = 1$
Nitrates							
Ammonium	NH_4NO_3	80·1	60·5	12·2°	(1·3)	67·0	9·2
,,	,,	,,	65·8	20·2°	(1·3)	60·0	7·6
Sodium	$NaNO_3$	85·1	80·6	10·0°	1·5	83·0	4·9
,,	,,	,,	87·8	20·0°	1·5	82·0	3·4
Calcium	$Ca(NO_3)_2$	164·1	121·0	18·0°	3·27	62·0	7·8
Strontium	$Sr(NO_3)_2$	211·6	70·8	20·0°	2·53	86·0	2·7
Barium	$Ba(NO_3)_2$	261·5	9·2	20·0°	1·97	98·8	0·23
Copper	$Cu(NO_3)_2$	187·6	117·0	18·0°	(2·5)	75·0	5·1
Lead	$Pb(NO_3)_2$	331·0	52·3	17·0°	(2·0)	97·2	0·7
Chlorides							
Ammonium	NH_4Cl	53·5	35·2	15·0°	1·82	81·0	4·4
Potassium	KCl	74·6	32·4	15·0°	1·9	86·0	3·1
Sodium	$NaCl$	58·5	35·8	15·0°	2·49	76·0	5·5
Calcium	$CaCl_2$	110·9	74·5	20·0°	5·3	43·0	10·8
Mercuric	$HgCl_2$	271·2	5·4	20·0°	(3·0)	98·9	0·20
Chlorates							
Potassium	$KClO_3$	122·6	7·2	20·0°	1·16	98·8	0·23
Sodium	$NaClO_3$	106·5	89·3	12·0°	2·3	70·0	7·7
Perchlorates							
Ammonium	NH_4ClO_4	117·5	20·0	(15·0°)	(1·5)	95·6	1·0
Potassium	$KClO_4$	138·6	1·7	(15·0°)	(1·2)	99·7	0·06
Sulphates							
Ammonium	$(NH_4)_2SO_4$	132·2	74·2	15·0°	1·85	83·0	3·9
Sodium	Na_2SO_4	142·3	13·4	15·0°	2·12	96·5	0·80
Magnesium	$MgSO_4$	120·4	36·2	20·0°	1·3	93·3	1·5
Zinc	$ZnSO_4$	161·5	50·9	15·0°	1·0	94·6	1·2
Aluminium	$Al_2(SO_4)_3$	342·4	36·1	20·0°	2·64	95·1	1·1
Ammonia alum	$Al_2(NH_4)_2(SO_4)_4$	474·6	6·25	15·0°	3·35	99·2	0·18
Sodium carbonate	Na_2CO_3	106·1	16·4	15·0°	2·46	93·3	1·5
Sodium bicarbonate	$NaHCO_3$	84·1	9·6	20·0°	(2·5)	97·1	0·54
Potassium carbonate	K_2CO_3	138·3	112·0	20·0°	2·73	65·0	6·6
Potassium sulphocyanide	$KCNS$	97·3	217·0	20·0°	1·75	50·0	9·5
Potassium chromate	K_2CrO_4	194·4	63·2	20·0°	2·74	85·0	2·9
Potassium bichromate	$K_2Cr_2O_7$	294·5	12·0	20·0°	(3·0)	99·3	0·14
Potassium ferrocyanide	$K_4Fe(CN)_6$	368·8	32·0	20·0°	2·86	98·5	0·29
Potassium permanganate	$KMnO_4$	158·2	5·2	15·0°	(1·5)	99·1	0·17
Mercury fulminate	$HgC_2N_2O_2$	284·6	1·8	12·0°	(1·0)	99·9	0·03
Ammonium oxalate	$(NH_4)_2C_2O_4$	124·2	6·9	25·0°	(1·1)	98·9	0·18
Cane sugar	$C_{12}H_{22}O_{11}$	342·2	197·0	15·0°	1·1	90·0	2·3
Urea	$CO(NH_2)_2$	60·1	79·0	20·0°	1·1	81·0	3·6

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there be not enough of it. The Home Office prescribes that these explosives shall pass the following test :

Test for liquefaction. A cylinder of length about equal to the diameter is cut from a cartridge, and the ends are cut flat. This is placed on end, without any wrapper, on a flat surface, and secured by a pin passing vertically through its centre. In this condition the cylinder is exposed to a temperature of 85° to 90° F. for 144 consecutive hours (six days and nights). During this exposure the cylinder must not diminish in height more than a quarter of its original height, and the upper cut surface must retain its flatness and the sharpness of its edge.

The German Railway Commission lays down that a complete cartridge shall be kept for five days at 30° C. (86° F.). No nitro-glycerine must exude, and after cooling the cartridge must be unchanged.

Wrappers. In the case of one particular brand of gelatinized explosives its great tendency to exude was traced by Hake to the use of wrappers of parchment paper made from wood pulp.[1] Such paper in the process of parchmentizing with sulphuric acid develops pores, through which the nitro-glycerine is drawn by capillary action and forms beads on the outside of the wrapper. Parchment paper made from cotton rags is free from this defect. In Germany wrappers of paraffined paper are used.

American dynamites, containing as they do ungelatinized nitro-glycerine absorbed in a comparatively small quantity of wood-meal together with a deliquescent salt, are particularly liable to exude. The matter was investigated in 1908 by the " Bureau for the safe Transportation of Explosives,"[2] and three different tests have been adopted :

Pressure test. (1) Pressure test. This is carried out in a glass tube 3 in. long and $1\frac{1}{8}$ in. internal diameter (sectional area 1 sq. in.). First 1·5 to 2 g. of cotton wool are placed in it, then 10 g. of the dynamite and then a second wad of 1·5 to 2 g. of cotton wool. The tube is placed upright on a vulcanite base, and a vulcanite disc is introduced into the tube above the upper wad, and on this a pressure of 80 lb. is exerted for 1 minute by means of a weight on a steel lever beam. The dynamite is then removed and weighed. The loss should not exceed 3 per cent. Dynamites which had absorbed much moisture were found to give up considerable amounts of nitro-glycerine in this test, as also did those with low proportions of wood pulp.

Keeping test. (2) Keeping test. A cartridge is kept in a vertical position for six days at a temperature of 40° C. The results of this test are generally in accordance with those given by the pressure test : if the latter shows an exudation of 5 per cent. or more, there is usually leakage at 40°. This, however, only applies to " straight " dynamites. If part of the wood-meal be replaced with kieselguhr, the explosive tends to give up much nitro-glycerine in the pressure test, but

[1] *J.S.C.I.*, 1905, p. 915.

[2] *Bureau of Explosives Report*, Nos. 2 and 4 ; *S.S.*, 1910, p. 213.

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does not sweat badly at 40°. On the other hand, if a coarse material such as sawdust be used instead of wood-meal, very little nitro-glycerine is lost in the pressure test, but there is much exudation at 40° as also under service conditions.

The objection may be raised that the pressure of 80 lb. per sq. in. is very much greater than any that will occur in practice: in a packing case the pressure on the material is not likely to exceed 1 lb. per sq. in. A test was therefore devised, in which the dynamite is exposed to centrifugal force. The pressure upon any part of the explosive is very moderate in this case, but if there be a film of too great a thickness on each particle of absorbent, part of the liquid is removed by the centrifugal force. The machine used has brass cups measuring $1\frac{5}{8}$ in. × $5\frac{1}{8}$ in. inside, and the bottoms of the cups describe a circle of 7 in. radius. The machine is worked by hand by means of a crank 7 ft. long, and it is enclosed in a heavy wooden box to reduce the risk to the operator. The sample is introduced into a glass tube exactly as in the case of the pressure test. It is then wrapped in cloth, and inserted into one of the cups, and the machine is rotated at 600 revolutions per minute for one minute. The loss should not be more than 3 per cent. **Centrifugal test.**

Sensitiveness or Danger in Handling

For general safety in dealing with explosives it is of great importance that they should not be too sensitive to blows or friction. A number of different tests have been devised for ascertaining the sensitiveness. A simple test consists of striking some of the explosive with a hammer; the severity may be varied not only by striking more or less violently, but also by placing the material on substances of different hardnesses. The late Dr. Dupré used a broom-stick, with which he gave a glancing blow, thus combining percussion and friction in the same test.[1] The explosive may be rubbed in a mortar, with or without the addition of sand or glass powder to increase the friction. Or it may be rubbed between pieces of wood covered with sand- or emery-paper. It may be shot at with a rifle; the severity of this test depends of course, on the velocity of the bullet; it is also made more severe if the explosive be supported on a surface inclined to the direction of impact, or if the layer of explosive be of considerable thickness.[2] In all these and similar tests the explosive should always be compared with a standard explosive of a like nature. The standard explosives and tests adopted by the German Railway Commission will be found in Appendix I.

The U.S. Bureau of Mines has adopted an apparatus for testing the sensitiveness of explosives to friction, consisting of a steel anvil and a steel shoe, which swings at the end of a long arm and can be loaded with different weights. **Friction test.**

[1] *See also* App. I., p. 591, Chlorate Explosives.

[2] Hess, *Ang.* 1904, p. 546.

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The anvil has a smooth face, and the shoe can be faced with fibre, steel, or other material. A few grammes of explosive are placed on the anvil, and the shoe is allowed to swing down from a known height and give it a glancing blow. The test is devised to represent what may happen in mining when a cartridge of explosive becomes lodged in a drill-hole and must be forced home by ramming.[1]

Falling weight test.

None of the above tests permit of the sensitiveness of the explosive being expressed by a definite figure, hence the advantage of the falling weight test,

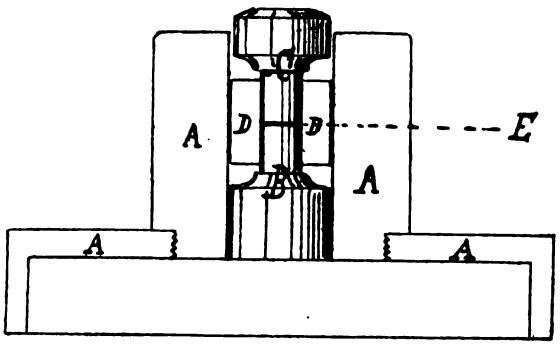

FIG. 77. Anvil, etc., of Falling Weight Apparatus

FIG. 78. Falling Weight Apparatus (E. A. Lentz, Berlin)

which allows the sensitiveness of quite different types of explosive to be compared. The evolution of the apparatus and method, in order to obtain constant and reliable results, was traced by Lenze at the 6th International Congress of Applied Chemistry,[2] and the matter was further dealt with by Kast at the 7th Congress in 1909. The following conditions must be fulfilled by the apparatus: The anvil must rest on a firm masonry foundation. The weight must not fall directly upon the explosive, but upon a bolt, C. (Fig. 77), which transmits the impact to the material under test, E, which rests on the anvil B. Both the bolt and anvil are made of hardened steel and can be ground down or renewed as soon as they become damaged. The sleeve, D, allows the stamp to move easily in a vertical direction, but permits no lateral movement, so that the explosive is subjected to impact only, and not to friction. The whole is held in position by the base, A. Fig. 78 shows the whole apparatus. Lenze and Kast use anvils and bolts with an

[1] *Bureau of Mines Bulletin* 66, 1913, pp. 15, 290.
[2] *Report*, vol. 2, p. 522; *S.S.*, 1906, p. 287.

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area of 0·5 sq. cm., but the apparatus of the American Bureau of Mines has a diameter of 1 cm. (area 0·785 sq. cm.), and at the 8th Congress it was resolved to adopt a diameter of 0·5 in. (1·27 cm., area 1·27 sq. cm.).[1] Weights of different sizes are used, but those of 2 and 10 kg. are the usual ones: the German Railway Commission tests all explosives with both of these. The results are influenced by the quantity of explosive used: in order to have a layer of the same thickness in every case it is better to measure the quantity rather than weigh it; the actual weight is generally 0·02 to 0·04 g., and the thickness of the layer about 1 mm. For the larger area adopted by the 8th Int. Congress the quantity of explosive is 0·05 to 0·1 g. If the quantity be increased it becomes less sensitive. In order to have the material in the state of maximum sensitiveness it should be dried for twenty-four hours over calcium chloride. It is usually wrapped in tin foil, and sometimes it is pressed into a flat tablet beforehand. The results are affected by the temperature at which the experiments are carried out: at 30° to 40° the length of fall is about 25 per cent. less than that required at 12° to 14°. The usual standard temperature is 18° to 20°; the anvil in some instruments is surrounded by a water jacket to facilitate the regulation of the temperature. The results are also affected by the physical condition of the explosive, the size of the grains, etc. A fresh quantity should be taken for each test, and the surfaces of the anvil and bolt carefully cleaned every time. This is specially important in the case of substances, such as picric acid, which form explosive compounds with iron.

The following classification of explosives according to their sensitiveness was given by Will at the 6th International Congress: [2]

		Length of fall cm.
Class I.	Cap compositions and substances of similar sensitiveness, which detonate on ignition and are not allowed to be transported	0–7
	Mercury fulminate	2
	Nitro-glycerine, dry	4
	Lead picrate	5
	Silver picrate	5
	Iron picrate	7
	Copper picrate	7
	Dinitro-glycerine	7
Class II.	Dynamites. Very sensitive to blows, burn vigorously or deflagrate when ignited. Danger of explosion present	7–25
	Guhr dynamite, plastic	7
	Blasting gelatine, plastic	12
	Blasting gelatine, frozen	12–15
	Gelatine dynamite, plastic	17
	Guhr dynamite, frozen	20
	Guhr dynamite from dinitro-glycerine, dry	25
	Blasting gelatine from dinitro-glycerine, dry	25

[1] *See* end of this chapter. [2] *S.S.*, 1906, 209.

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		Length of fall cm.
Class III.	About	26–100
	(*a*) Black powder. Not very sensitive to blows. Easily ignited. With safety fuse deflagrates. Danger of explosion not absent.	
	Sporting powder	70
	Blasting powder	85
	Black powder, coarse grain	100
	(*b*) Chlorate explosives. Moderately sensitive to blows, difficult to light, not ignited by safety fuse. Danger of explosion not absent.	
	Cheddite 60	32
	Cheddite 41	36
	(*c*) Aromatic nitro-compounds. Sensitive to blows. Difficult to light, not ignited by safety fuse. Danger of explosion not absent.	
	Tetranitro-methylaniline	40–65
	Hexanitro-diphenylamine	40
	Trinitro-benzene	40–50
	Trinitro-toluene	57–180
	Ammonium picrate	80
	Sodium picrate	80
	Trinitro-dimethylaniline	95
	Trinitro-cresol	30
	Picric acid	35–95
	(*d*) Nitro-cellulose with 15 per cent. water. Little sensitive to blows. Difficult to light. Not ignited by safety fuse. Danger of explosion not absent.	
	Gun-cotton, with 15 per cent. water	85
	Collodion cotton, with 15 per cent. water	100
	(*e*) Smokeless powders. Fairly sensitive to blows. Comparatively easy to light, burns rapidly or deflagrates when ignited with safety fuse. Danger of explosion almost absent.	
	Cube powder (nitro-glycerine)	20–30
	Sporting powder	30–45
	Rottweil flake powder	32
	Flake powders	30–54
Class IV.		100–200
	(*a*) Safety (in handling) explosives. Little sensitive to blows. Difficult to light, not ignited by safety fuse. Danger of explosion absent.	
	Roburite 1a	105
	Ammon-carbonite	110
	Astralite	110
	Donarite	110
	Fulmenite, Wetter-fulmenite	more than 180
	Rottweil safety powder	,, 180
	Anagon-sprengpulver	,, 180

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	Length of fall cm.
(*b*) Aromatic nitro-compounds with lower nitrogen-content than Class III (*c*). Little sensitive to blows. Difficult to light, not ignited by safety fuse. Danger of explosion absent.	
Dinitro-benzene	120
Dinitro-phenol	150
Trinitro-xylene	170
Trinitro-naphthalene	175
(*c*) Nitro-cellulose with over 20 per cent. water. Insensitive to blows. Difficult to light, not ignited by safety fuse. Danger of explosion absent.	
Gun-cotton, with 20 per cent. water	more than 185
Collodion cotton, with 20 per cent. water	,, 185

These results were obtained with a weight of 2 kg. falling on to a steel bolt resting on 0·1 gr. of the substance, which was previously dried at 40°, except where otherwise stated. These results are in fairly good agreement with those obtained by others,[1] but for the more insensitive explosives it is better to increase the weight rather than have falls as long as 1·8 metres. The results with frozen blasting gelatine are not in agreement with those obtained in England with thicker layers.[2]

The following Table of the sensitiveness of various explosives when tested with different weights gives the results published by Bichel [3] and Brunswig [4]:

Explosive	Composition	Fall in cm. required to cause explosion						
		Falling weight in kilogrammes						
		0·1 kg.	0·25 kg.	0·5 kg.	1·0 kg.	2·0 kg.	5·0 kg.	20 kg.
Nitrogen iodide	NI_3	(*b*) 5						
Mercury fulminate	$HgC_2N_2O_2$	5–10	(*b*) 5					
Nitro-glycerine	$C_3H_5(NO_3)_3$	5–10	(*b*) 5					
Guhr dynamite	75 N/G 25 Guhr	5–10	(*b*) 5					
Gelatine dynamite	63·5 N/G 1·5 N/C 27·0 $NaNO_3$ 8·0 Wood-meal	5–10	(*b*) 5					

(*b*) means below.

[1] *See* Bichel, *Marine-Rundschau*, 1905, p. 1345; *S.S.*, 1906, 14; Zschokke, *Militarische Sprengtechnik*, 1911.

[2] *See* Chap. xvii.

[3] *Marine-Rundschau*, 1905, p. 1345.

[4] *Explosivstoffe*, 1907.

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Explosive	Composition	Fall in cm. required to cause explosion						
		Falling weight in kilogrammes						
		0·1 kg.	0·25 kg.	0·5 kg.	1·0 kg.	2·0 kg.	5·0 kg.	20 kg.
Dinitro-glycerine	$C_3H_5(NO_3)_2OH$	10–15	5–10	(*b*) 5				
Gel. dyn. made from it	63·5 D/n/G 1·5 N/C 27·0 $NaNO_3$ 8·0 Wood-meal	30–35	15–20	5–10	(*b*) 5			
Pot. Chlorate and sulphur	$KClO_3$ + S	15–20	10–15	5–10	(*b*) 5			
Gun-cotton, dry		30–40	15–20	5–10	5–10	5–10	(*b*) 5	
Flake powder .	Gelatinized N/C	40–50	20–30	10–15	10–15	10–15	5–10	(*b*) 5
Gun cotton, wet	15 per cent. H_2O	(*a*) 200	70–80	15–20	10–15	10–15	5–10	(*b*) 5
Black powder	75·0 KNO_3 10·0 S. 15·0 Charcoal		(*a*) 200	190–200	100–110	30–40	5–10	(*b*) 5
Picric acid, crystalline	$C_6H_2(NO_2)_3OH$			(*a*) 200	190–200	100–110	50–60	(*b*) 5
Picric acid, compressed	$C_6H_2(NO_2)_3OH$				(*a*) 200	140–150	80–90	(*b*) 5
Trinitro-toluene, crystalline	$C_6H_2(NO_2)_3CH_3$			(*a*) 200	180–190	90–100	50–60	(*b*) 5
Trinitro-toluene, compressed	$C_6H_2(NO_2)_3CH_3$				(*a*) 200	150–160	80–90	(*b*) 5
Gelatine-carbonite	25·3 N/G 0·7 N/C 41·5 NH_4NO_3 6·9 Glyc. jel. 25·6 NaCl	80–90	20–30	5–10	5–10	5–10	(*b*) 5	
Kohlen-carbonite	25·0 N/G 34·0 KNO_3 1·0 $Ba(NO_3)_2$ 38·5 Flour 1·0 Tan 0·5 Soda	(*a*) 200	50–60	20–30	20–30	20–30	5–10	(*b*) 5
Carbonite II .	30·0 N/G 24·5 $NaNO_3$ 40·5 Flour 5·0 $K_2Cr_2O_7$	60–70	30–40	10–20	10–20	10–20	(*b*) 5	

(*a*) means above, (*b*) below.

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Explosive	Composition	Fall in cm. required to cause explosion						
		Falling weight in kilogrammes						
		0·1 kg.	0·25 kg.	0·5 kg.	1·0 kg.	2·0 kg.	5·0 kg.	20 kg.
Ammon-carbonite	4·0 B/G 82·0 NH_4NO_3 10·0 KNO_3 4·0 Flour	(*a*) 200	(*a*) 200	170–180	100–110	40–50	15–20	(*b*) 5
Donarite	3·8 N/G 0·2 N/C 80·0 NH_4NO_3 12·0 T/n/T 4·0 Flour			(*a*) 200	120–130	60–70	15–20	(*b*) 5
Grisounite couche	95·5 NH_4NO_3 4·5 T/n/n				(*a*) 200	140–150	70–80	(*b*) 5
Roburite II	71·5 NH_4NO_3 5·0 KNO_3 6·0 Flour 0·5 $KMnO_4$ 5·0 NaCl 12·0 T/n/T				(*a*) 200	70–80	50–60	(*b*) 5

(*a*) means above, (*b*) below.

The determinations were carried out with quantities of 0·1 gr. wrapped in tin-foil.

The U.S. Bureau of Mines has recently adopted a much larger apparatus in which a weight of 200 kg. is used and can be dropped as much as 7·5 metres. In this apparatus 20 g. of explosive are used each time. It is claimed that with this larger charge the results are more reliable and represent more closely the relative sensitiveness of explosives to direct impact. They are not parallel to those obtained with a smaller apparatus.[1]

Sensitiveness to detonation.

Sensitiveness to detonation is ascertained by firing cartridges with detonators of varying strength to discover the weakest that will detonate it completely. The action of fulminate of mercury and similar substances resembles that of a blow rather than of a flame, so the results of this test are on the whole parallel with those obtained by the falling weight test. Explosives for use in coal-mines when tested for safety are fired into the testing galleries without any stemming, so that it is necessary that they should detonate completely when fired with a No. 7 or 8 detonator unconfined. Explosives for military purposes also must detonate unconfined, but those usually used, trinitro-toluene,

[1] *Bureau of Mines Bulletin* 66, 1913, pp. 17, 287.

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picric acid, wet gun-cotton, require special detonators or a priming of some powerful explosive.

The detonators used for this test must, of course, be reliable and uniform in strength. The density of the explosive greatly influences its sensitiveness to detonation: the denser it is, the more difficult it becomes to detonate it. At a high density many ammonium nitrate and chlorate explosives become practically inexplosive; even if detonation be started by means of a powerful priming, it is not propagated throughout the mass, but dies away leaving part of the explosive unconsumed. Well crystallized substances are generally less difficult to detonate when reduced to powder, but are then more sensitive to blows. From a blow the fine material apparently escapes without being subjected to much shock, but the effect of the detonator is concentrated on a smaller mass of material.[1] If unconfined a finely powdered explosive may be scattered without being detonated completely, but if confined it is more easily detonated than the coarse crystalline material. Frozen nitro-glycerine explosives are much less sensitive to detonation, whereas to blows under some conditions they are more sensitive.

Effect of temperature.

At high temperatures explosives are considerably more sensitive; conversely their sensitiveness is reduced by cooling them. The following Table shows the quantity of fulminate in grammes required to detonate various explosives when cooled to about −80° by means of solid carbon dioxide and acetone, or to about −190° with liquid nitrogen.[2]

Explosive	Density	Grammes fulminate required		
		Ordinary temperature	−80°	−190°
Fulminate	1·20	$<$ 0·25	—	1·0
Blasting gelatine	—	$<$ 0·25	0·25	1·0
Cheddite No. 2	1·00	0·25	0·75	$>$2·0
Picric acid	0·90	0·25	1·0	$>$2·0
Gun-cotton	0·40	0·25	0·25	$>$2·0

In these experiments the detonator was cooled as well as the explosive, and the effect is partly due to reduced efficiency of the detonators at low temperatures. It was found that if the detonator were cooled to −190°, it was necessary for it to contain 1 g. of fulminate in order to detonate uncooled picric acid (density 1·0), whereas with the detonator at the ordinary temperature 0·25 g. sufficed.

[1] *See* Hess, *Ang.*, 1904, p. 546.

[2] A. Kling and D. Florentin, *P. et S.*, vol. xvii., 1913, p. 145.

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Transmission of detonation.

An allied property is that of transmitting detonation from one cartridge to another across an intervening space by "influence." The more sensitive an explosive is, the greater is the distance at which it can be exploded, but the distance is also affected by the violence of the impulse given by the first cartridge, which again depends to a considerable extent upon the velocity of detonation. Another factor is the nature of the surface on which the cartridges are resting. They are often placed on a steel rail; on soft ground the distance is less, and if they are suspended in the air less still. The last arrangement offers the advantage of a fairly constant universal medium, but the objection may be raised that the conditions are fundamentally different from those prevailing in practice; the relative values for explosives of similar type probably remain much the same, however. If the two cartridges are placed in a roll of paper, the detonation is transmitted over a greater distance than if they are quite unconfined. A simple method of determining the distance of transmission is to set out a row of small cartridges at increasing distances and ascertain how many of them explode when the end cartridge is detonated. The results depend on the density of the explosive among other factors; for on the one hand an increase in density increases the velocity of detonation, but on the other it makes the explosive less sensitive. With cartridges of greater diameter the transmission is naturally better. These tests are carried out with the cartridges arranged end on to one another. It is important that the transmission shall not be too poor, because this involves danger that the whole of a charge in a bore-hole will not be detonated, if for any reason the different cartridges are separated from one another by moderate intervals. Some explosives transmit so badly when frozen that detonation is incomplete even when there is no break in the continuity of the charge.

Total or partial failure to detonate is a frequent cause of accidents, as the explosive is liable to go off during subsequent handling of the material that is being blasted. Accidents also occur in drilling fresh holes near unexploded charges. The "P.P. apparatus" has been devised to obviate this danger by safely withdrawing the detonator and replacing it.[1]

Some interesting experiments were made by Comey on the velocity with which detonation is transmitted through air from one cartridge of explosive to another.[2] The explosives used were American "straight dynamites" of various strengths. Half sticks were wrapped in paper leaving one end exposed, and these were laid on the ground with the exposed ends facing one another. Into these ends were inserted detonators, which were connected together by detonating fuse, so that the time of transmission could be measured by Dautriche's method. The following results were obtained.

[1] *See A.R.* 1913, pp. 42, 43.

[2] *Report of 7th Int. Cong. Appl. Chem.*, vol. iiib., p. 30.

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Strength of Dynamite	Normal Velocity of Detonation	Velocity of Transmission of the Wave of Detonation through the Air								Limit of Sensitiveness
		5″ (127 mm.)	10″ (254 mm.)	15″ (381 mm.)	20″ (508 mm.)	25″ (635 mm.)	28″ (711 mm.)	30″ (762 mm.)	40″ (1016 mm.)	
Per cent.										
60	5795	5346	5224	—	4295	—	—	3852	2733	48″ (1219 mm.)
40	4796	4500	4196	—	3537	—	—	2714	2253	40″ (1016 mm.)
30	4311	—	3489	—	3159	—	—	—	—	42″ (1067 mm.)
25	3349	3426	3502	3250	2939	2572	2357	—	—	28″ (711 mm.)
20	3297	—	3103	—	2665	—	—	—	—	32″ (813 mm.)
60	—	—	5260	—	4372	—	—	3567	whole sticks	
40	—	—	4610	—	3791	—	—	2908	,,	,,

If these results are recalculated so as to give the velocities over each interval instead of the mean velocity from the start, the following are the figures :

Strength of Dynamite	Normal Velocity of Detonation	0–10″	10–20″	20–30″	30–40″
per cent.					
60	5795	5183	3650	3175	1460
40	4796	4215	3110	1710	1490
30	4311	3489	2880	—	—
25	3349	3503	2560	1733[1]	—
20	3297	3103	2340	—	—
60	5795	5260	4390	2620	—
40	4796	4610	3220	1990	—

[1] 20–28″.

Considering that each result was obtained with a different cartridge the figures are fairly regular. The wave set up in the air apparently starts with about the same velocity as that of the detonation of the explosive, and then the velocity decreases at the rate of about 50 metres per second for every cm. traversed.

The " limits of sensitiveness " given by Comey are high, and were no doubt affected by the presence of a detonator in the end of the second cartridge ; they represent in fact the distances at which a detonator is fired by the explosives. The standard dynamite of the Pittsburgh Testing Station, which has the composition :

Nitro-glycerine	40
Sodium nitrate	44
Wood pulp	15
Calcium carbonate	1

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transmits to another cartridge with no detonator only over a distance of 17 inches, both cartridges being suspended in the air. Carbonites, which contain less nitrate and more wood-meal and other constituents transmit only to distances of 2 inches to 9 inches. An explosive consisting of ammonium nitrate with 6·6 per cent. trinitro-toluene and 4·2 per cent. nitro-naphthalene would not transmit with certainty even to ½-inch, but another ammonium nitrate explosive transmitted to 2 inches.[1]

Sensitiveness to heat.

The danger in the handling and transport of an explosive depends very largely on its behaviour when exposed accidentally to heat, flame or spark. Will's classification on pp. 345 to 347 is based very largely on this. An explosive which catches fire easily, or explodes when it comes in contact with fire, is much more dangerous than one that can only be lit with difficulty and then burns quietly. As in the case of sensitiveness to blows and friction these properties are of even more importance in explosives intended for military use than in ordinary mining explosives. Kast [2] gives the following tests :

Behaviour at Temperatures near the Ignition Point. The ignition point is ascertained by the method given in Appendix I, p. 558. Then in a second experiment the bath is heated to this temperature with the empty test-tubes in it, and the explosive is only then introduced into them. In a third experiment the bath is heated to a temperature 10° above the ignition point, and in a fourth 10° (or 20°) below it. Every test is repeated two or three times. The time until the material puffs off is taken as the measure of its sensitiveness. Of black powder, ammonium nitrate and chlorate explosives 0·5 g. is taken each time ; of dynamites or nitro-celluloses 0·1 g.

Behaviour Towards Direct Ignition. A small quantity (5 to 10 g.) is ignited on an iron plate with a burning splinter of wood, a second with a red-hot iron wire, and a third by throwing it into a red-hot iron basin, and it is observed whether it burns slowly, or fast, or puffs off. The test is made more severe if the explosive be heated beforehand to a high temperature (100° to 200°), and is then ignited.

A portion of 3 g. of the explosive is placed loosely in a short test tube, and a piece of safety fuse is inserted into the middle of it. It is observed whether the material deflagrates, when the fuse burns down to it.

Finally a considerable quantity of the explosive packed in a box is introduced into a fierce fire.

It is thus ascertained whether the explosive is liable to explode. Black powder and similar explosives behave the worst under these circumstances ; then follow dynamite, chlorate explosives, then the nitro-compounds such as picric acid, and finally the practically incombustible ammonium nitrate explosives.

The tests adopted by the German Railway Commission are given in Appendix I. The Table on p. 354 gives the results of the standard explosives :

[1] *Bureau of Mines Bulletin* No. 15. [2] *Spreng- und Zündstoffe*, p. 1017.

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Standard explosive	Safety fuse test	Red-hot iron basin	Ignition point in metal bath	In iron box in fire
Donarite . .	No ignition	No explosion	(*a*) 250°	No explosion
Picric acid . .	,,	,,	300°	Burns rapidly. No explosion
Tetranitro-methylaniline	,,	,,	190°	Burns with occasional puffs
Cheddite . .	,,	,,	(*a*) 200°	Slight deflagration
Silesia . .	,,	,,	(*a*) 200°	Vigorous deflagration
Blasting saltpetre	Burns. No detonation	Burns rapidly. No detonation	300°	
Black powder (sporting)	,, ,,	Puffs off at once. No explosion	300°	
Guhr dynamite .	Ignites. No explosion	Burns without explosion	207°–215°	
Blasting gelatine	,, ,,	,, ,,	207°–211°	

(*a*) means above.

Temperature of ignition.

In order to determine the temperature of ignition a small sample of the explosive, usually 0·1 g., is placed in a small test-tube, which is then tightly corked and placed in a paraffin bath at 100°. The bath is now stirred and heated so that the temperature increases 5° per minute. The temperature is noted at which the sample explodes. The following are the lower limits of the explosion temperatures for satisfactory samples, as required by the United States Ordnance Department : [1]

Nitro-cellulose	186°
Nitro-cellulose powder	177°
Nitro-glycerine ,, ...	170°

The results are found to be reliable when the explosive is either very good or very bad. Variations in the results may be caused by differences in manipulation, especially in the rate of raising the temperature.

Fig. 79 shows an apparatus that is used in Spain for determining the temperature of ignition. The copper bar, *a*, has a circular enlargement at one end, in which there are five holes ; the central one, *F*, contains mercury, in which the bulb of a thermometer is immersed ; in each of the others is placed a copper tube containing 0·1 g. of the explosive to be tested. The bar is supported on a stand, and is heated by means of burners placed underneath it : the rate of heating can be regulated by moving the burners. The explosive

[1] *See* Sy, *J. Frank. Inst.*

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in tube *b* explodes first, then *c* and *d*, and finally *e*. The mean of the readings of the thermometer when the explosions occur is taken as the temperature of ignition. If this temperature be above 180° the explosive (presumably

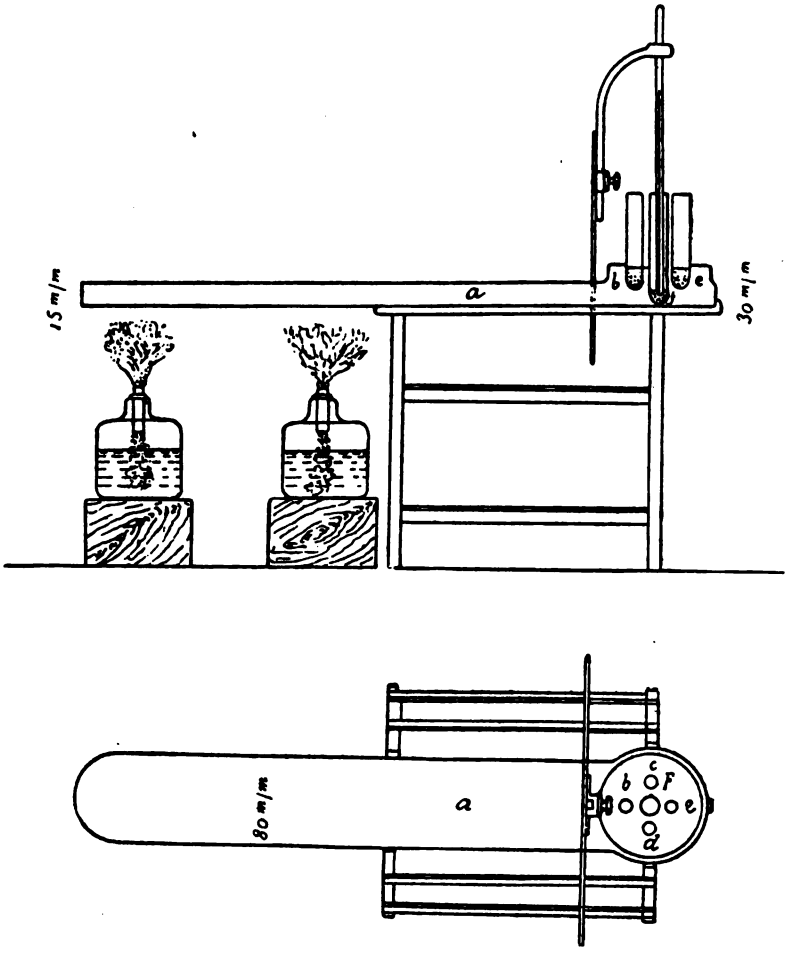

FIG. 79. Apparatus for Determining the Temperature of Ignition

nitro-cellulose powder) is considered good; if between 178° to 180° it is serviceable; if between 176° and 178° it is sentenced to immediate expenditure; if below 176° to destruction.[1]

The method adopted by the German Railway Commission for determining the temperature of ignition is given in Appendix I, pp. 588, 590, as also a method for ascertaining the time required for igniting a small quantity at a temperature

[1] *First Report of Intern. Commission, Brussels*, 1908, p. 60.

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of 145° (p. 591). Finzi has given the results of a considerable number of determinations of the temperature of ignition of nitro-cellulose in various states of stability, and also of smokeless powders.[1]

Dupré found that determinations of the temperature of ignition gave fairly concordant results, but that they were influenced by many conditions, such as the temperature at start, the rate of rise of temperature, the size of the tube, and the weight of explosive. Samples of very different stablity do not give very different results.[2]

International Committee.

The International Committee on Tests for Explosives has adopted the following methods for the examination of commercial blasting explosives, to ascertain whether they are safe enough for transport.[3]

I. *Preliminary Test.* Two portions, each of 10 g. of the explosive not dried, are placed in glass capsules loosely covered, 25 mm. in diameter and 50 mm. high. They are placed in an oven heated to 75°, where they remain for forty-eight hours. No decomposition must have occurred in the explosive, nor must there be any notable change in its appearance or smell. In the case of nitro-explosives there must be no formation of red fumes.

II. *Falling Weight Test.* Equal weights of the explosive under examination previously powdered and dried, on the one hand, and of pure picric acid powdered and dry, on the other, are tested in the same apparatus under identical conditions. The portions taken, 0·05 to 0·1 g. each, are placed on a steel anvil in the form of a layer 1·27 cm. ($\frac{1}{2}$-inch) in diameter. On top of the explosive is placed a cylinder of tempered steel, 1·27 cm. in diameter and the same in height. Ten consecutive tests are carried out with each of the explosives in order to determine the mean height of fall necessary to cause explosion.

To be considered insensitive to shock, the explosives must not be more sensitive than pure powdered picric acid.

II*b*. *Friction Test.* The explosive, placed in an unglazed porcelain mortar gently warmed (20° to 30°), must not prove more sensitive than pure powdered picric acid submitted in the same apparatus to identically the same test.

III. *Sensitiveness to Ignition.*

(*a*) Fuse Test. Three g. of the powdered explosive are placed in a glass test-tube. By gentle tapping the substance is given an even surface. Then a slow-burning fuse (1 cm. per second) is introduced. The test is repeated twice. If ignition occurs, the substance is classified as a deflagrating powder or a readily inflammable explosive.

[1] *Gazzetta Chimica Italiana*, 1909, p. 549 ; *S.S.*, 1910, p. 153. [2] *A.R.*, 1904, p. 28.

[3] *Report of 8th Inter. Cong. Appl. Chem.*, vol. 25, p. 261. The Committee published an English version of the Instructions, but I have preferred to make a translation of the original French.

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(*b*) Red-Hot Iron Basin Test. If the explosive has passed the last test without igniting, it is submitted in this test to a high temperature to make sure that it is not liable to explode when exposed to fire.

A hemispherical iron basin 12 cm. in diameter and 1 mm. thick is heated red hot on a burner; a small quantity (0·5 g.) of the powdered substance is first introduced, then if there be no explosion the quantity is increased up to 5 g. The test is carried out three times.

(*c*) The Red-Hot Iron Test is to ascertain the inability of safety explosives to burn. After some preliminary trials with small quantities to ascertain that the product has comparatively little tendency to burn, 100 gr. of the explosive are placed on an asbestos card; the end of an iron bar 15 mm. in diameter, heated to a cherry red (about 900°) for a length of 10 cm., is then brought into contact with the explosive. The substance must only burn slowly, without exploding at all, and the flame must die out when the source of heat is withdrawn.

The effect of these three groups of tests is to divide explosives into three classes:

(1) Explosives sensitive to mechanical action will give results inferior to picric acid in tests II and II*b*; this class includes dynamites and certain chlorate explosives.

(2) Gunpowder and similar explosives will fail in test III*a*.

(3) Ammonium nitrate explosives will generally pass tests III*b* and *c*, as also will other explosives that possess a high degree of safety in transit.

If an explosive after passing tests II, II*b* and III*a* explode in the red-hot basin (III*b*), it will be necessary to reduce it to class 1. But this is only likely to occur with certain types, which are but little used.

An explosive which having passed tests II, II*b*, III*a* and III*b*, is found to burn with violence in test III*c*, would have to be classed with gunpowder (class 1), or be placed in a sub-class between the second and third classes.

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CHAPTER XXVII

THE PRESSURE AND HEAT OF EXPLOSION

Heat of explosion : Calorimeters : Corrections : Means of ignition : Volume of gas : Pressure : Rodman's gauge : Crusher gauge : Rifle pressures : Shot-gun pressures : Recording pressure gauges : Relation of pressure to gravimetric density : Calculation of temperature from heat of explosion : Specific heats of gases : Of solids : Products of explosion : Formation of methane : Of ammonia : Carbonates : Carbon : Aluminium : Calculation of temperature from pressure : Direct measurement of temperature : Examples of calculations

Heat of Explosion

WHEN an explosive is fired, heat is always liberated, and the amount of this heat per unit weight of explosive is one of the most important factors governing the power of the explosive. Many explosives liberate practically the same amount of heat when exploded under very different conditions, others show slight variations, which, however, can be explained.

Calorimeters. Calorimeter bombs for measuring directly the heat of explosion differ from those used for ordinary thermo-chemical work in that they have to be much stronger in order to withstand the high pressures generated. Berthelot in his early experiments used a light bomb in which he could only deal with a small quantity of explosive. Sarrau's " éprouvette calorimétrique," although it had a capacity of 300 c.c. could only take a charge of 3 g., because the walls were not very thick.[1] Noble and Abel in their classical *Researches on Explosives* were the first to use a very strong bomb (Fig. 80), in which as much as 500 g. of gunpowder could be exploded at a density exceeding 1.[2] The plug, C, carries an arrangement for firing the powder by means of a wire heated to incandescence by electricity ; K carries a crusher gauge for measuring the pressure generated, and E enables the gaseous products of explosion to be collected, measured and analysed. Afterwards the same investigators used the calorimeter shown in Fig. 81. Two bombs were used with this : one had a capacity of 32·5 c.c. and took 10 to 13 g. of gunpowder, the other had a capacity of 118·8 c.c. and took 26 g.[3]

Many modern explosives, especially those containing ammonium nitrate, can be exploded only by means of a detonator containing a fairly powerful

[1] *P. et S.*, vol. vii. [2] *Trans. R.S.* 1875. [3] *Trans. R. S.* 1879.

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charge of fulminate of mercury or similar substance. In order that the heat due to the detonator may be small in comparison with that of the explosive, it is desirable to fire a large charge. Bichel and Mettegang, not wishing to make their bomb too thick and heavy, enlarged its capacity to 30,000 c.c. It is bottle shaped, and has walls about 13 mm. thick, and weighs about 70 kg. This is placed in the cylindrical copper vessel shown in Fig. 82 containing a

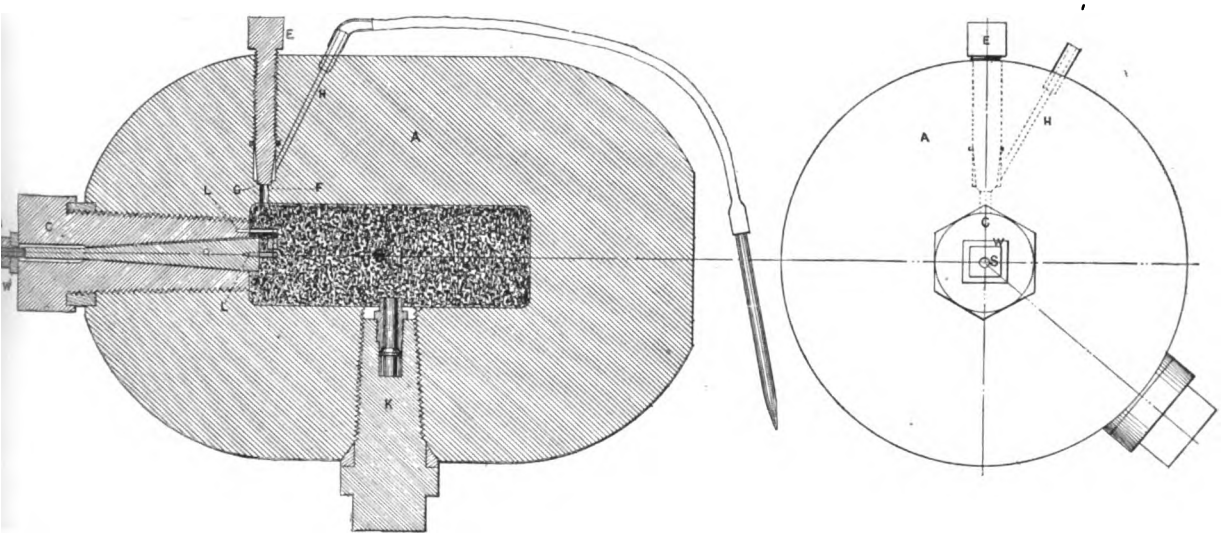

FIG. 80. Noble and Abel's Bomb

known volume of water, which is kept stirred mechanically ; the copper vessel is placed inside the wooden tub to insulate it and protect it from draughts. Into the water dips a thermometer, which can be read to 0·001° : there is an arrangement for knocking this continually to prevent the mercury column sticking. The charge of explosive is suspended in the middle of the bomb. It is of course necessary to observe the precautions usual in calorimetric work. The calorimeter takes a charge of 100 g. of high explosive, or double the quantity of black powder.

For studying the explosion of high explosives at high densities of charging there is at the Centralstelle, Neubabelsberg, a strong bomb of nickel steel with a capacity of about 45 c.c., which can take a charge of 20 g. All such bombs require to be very carefully designed and made, for if there be the least leak, the escaping gas at the high temperature and pressure will wash away the metal and perhaps make the bomb quite unserviceable. On the other hand, the closing plugs must not jam so tightly that the bomb cannot be opened.

Corrections. The rise of temperature multiplied by the sum of the quantity of water in the calorimeter and the water equivalent of the apparatus and of the

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contents of the bomb, is the amount of heat produced by the explosion of the charge. But certain corrections have to be applied to obtain the true value. Under the experimental conditions the water produced is practically all condensed to liquid in the bomb, but when an explosive is actually used all the water is generated in the state of vapour, consequently the latent heat of condensation of the water must be subtracted from the heat found. Again, if there be any solid bases formed in the reaction, they will be converted by the carbonic acid present into carbonates or bicarbonates, and the heat liberated in this change must also be subtracted, as also the heat of solution of any soluble solids.

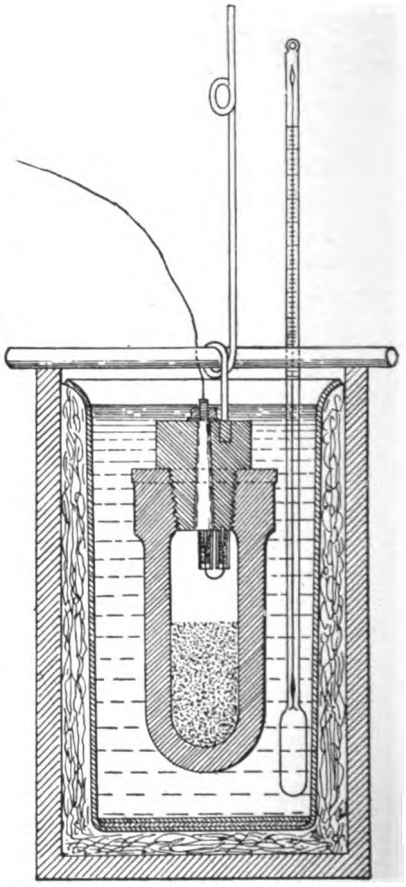

Fig. 81. Noble and Abel's Calorimeter

The condensation of 1 mol. of water liberates 10·9 large calories according to Berthelot, or 10·4 at a temperature of 18° according to Thomsen. The formation of the bicarbonates is shown by the equations :

$$Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3 + 31{\cdot}0 \text{ Cals.}$$
$$K_2CO_3 + CO_2 + H_2O = 2KHCO_3 + 35{\cdot}4 \text{ Cals.}$$

the water being in the form of gas.

Means of ignition.

Allowance must also be made for the heat produced by the means of ignition. Unfortunately this depends not only on the nature of the igniter, but also in many cases on the composition of the gases given off by the explosion of the substance under investigation. If these gases contain an excess of oxygen, the heat due to a detonator, for instance, is much higher than if it be detonated by itself, or used for an explosive that produces a reducing atmosphere. Thus it was found at the Schlebusch works [1] that a No. 3 detonator (containing 0·255 g. fulminate and 0·045 g. potassium chlorate) gave 0·166 Cal. in a reducing atmosphere and 0·791 in an oxidizing one. The increase is due not only to the conversion of the carbon monoxide into dioxide, but also to the oxidation of the copper of the detonator and the insulating material of the wires. Hall gives the heat produced by a No. 7 detonator (1·5 g. charge) as 0·86 Cal. evidently fired in the absence of free oxygen ; [2] Bichel for a No. 8 detonator (2 g.) found 1·381 Cals.

[1] *S.S.*, 1907, pp. 281, 306.

[2] *Bureau of Mines Bulletin* 15, p. 111.

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The volume of the gases formed can be estimated in various ways. If the explosion has been carried out in a capacious vessel, so that the density is only

Volume of gas.

FIG. 82. Bichel and Mettegang's Calorimeter with Accessories

about 0·01, it can be deduced from the pressure after the vessel and the products have cooled to the ordinary temperature ; but if this remaining pressure be too high, the estimation is somewhat uncertain. It can also be calculated from their weight, as determined by weighing the vessel before and after allowing the gases to escape ; if the density of the gases at atmospheric pressure be determined either by actual weighing or by calculation from the composition,

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the volume can then be deduced. Or again the whole of the gas can be collected and measured. As the volumes are large, special appliances are required for this; their design depends upon the magnitude of the charges to be dealt with.

The gases are analysed by the ordinary methods. The water can be driven out of the bomb by heating it in a bath of hot water and drawing a current of dry air through. The greater part of the water can be collected in a cold glass bulb and weighed, and the remainder can be absorbed in tubes filled with calcium chloride or sulphuric acid. It may be necessary to add to the volume of carbon dioxide found, that absorbed by the bases formed by the explosion, as noticed above. The gases usually formed are CO_2, CO, H_2, N_2, O_2, CH_4, and sometimes other hydro-carbons, especially if the explosive contain metallic aluminium. Ammonia and oxides of nitrogen are also produced sometimes in small quantities, but are not generally estimated, partly on account of the difficulty of determining them without loss.

If the products of explosion be known, the heat liberated can be calculated from their known heats of formation and those of the original constituents of the explosive. The sum of the former minus the sum of the latter is the heat of explosion. In Appendix II are given the heats of formation of the principal materials that occur in explosives, as well as other data that are required for these calculations. The calculations made in this way agree well with the results obtained in the bomb calorimeter.

Pressure

The occasional bursting of fire-arms must have called attention early to the great pressure that is generated when gunpowder is fired in a confined space, but it was long before this pressure could be measured with anything approaching accuracy. In the eighteenth century Count Rumford attempted to measure it by exploding the powder in a small vessel closed by a ball, and ascertaining the weight which sufficed to prevent the ball being lifted, but he obtained results which were many times higher than they should have been.

Rodman's gauge. The first instrument that gave results approaching accuracy was the gauge invented in 1861 by Major Rodman of the United States army. A hole was bored in the wall of the gun or vessel, and the gauge was screwed in so that the pressure of the gases could act upon the base of a small piston, which forced a knife edge into a disc of copper. The force required to produce depressions of various depths in the copper was determined by actual trial, and hence the pressure of the gases could be calculated.

Crusher gauge. The crusher gauge, which is very largely used at the present day, is merely a development of Rodman's gauge, the principal difference being that small cylinders of copper are crushed between two flat surfaces, and from the diminu-

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tion of height the pressure is deduced. The crusher gauge is shown in Fig. 83 : C is the piston ; the end next the powder chamber is protected by the gas-check, D, which prevents the gases escaping past it; the copper crusher, A, is held in position by a small spring ; the whole is screwed into the wall of the gun. When it is not desired to make a hole in the fire-arm, the pressure in the chamber can be ascertained by placing a small crusher gauge bodily inside the chamber at the back of the charge. On firing, this is thrown out of the muzzle a short distance, and is afterwards picked up and the copper is taken out and measured. Experience has shown that certain precautions are necessary to obtain reliable results : the end of the piston should not be far above the

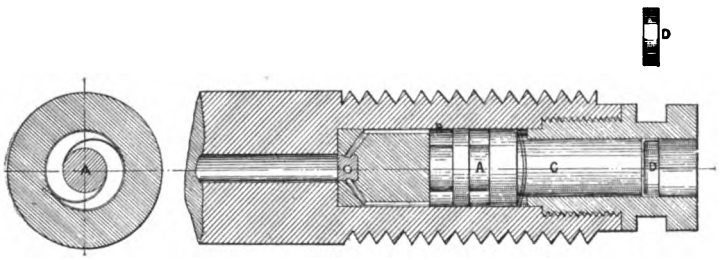

FIG. 83. Crusher Gauge (from *Artillery and Explosives*, by Sir A. Noble)

interior surface of the wall of the gun, else the gases in rushing up the empty channel acquire great momentum, which they transmit to the piston, causing the copper cylinder to be crushed too much. The copper should be compressed beforehand with a static pressure only slightly less than that which it is to undergo in the actual test, else the momentum acquired by the piston will in a similar way make the result too high.

Rifle pressure.

For measuring the pressures developed by rifle cartridges use is made of a special gun so arranged that, on firing, the base of the cartridge case presses back on a piston, which in turn presses on to the copper cylinder. The cartridge case is dipped beforehand into lubricating oil so that no appreciable amount of force shall be lost by friction.

Shot-gun pressures.

Whereas in rifled fire-arms the chamber pressures are 10 to 20 tons per sq. in., in shot-guns they are generally between 2 and 4 tons per sq. in. : the mechanism can therefore be made lighter and the gas-check can be omitted, but special difficulties are introduced by the great variations which are liable to occur in the pressures generated by smokeless shot-gun powders, which render it impossible to submit the crusher to a pressure closely approaching that to which it will be subjected. In England lead crushers are generally used instead of those made of copper, as these do not require to be pressed beforehand, and they have been found to give satisfactory results. They are standardized by subjecting a proportion of them to an impact test, the diminu-

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tion of height being ascertained after allowing a standard weight to fall on one from a standard height. The lead crushers are supplied by Eley Bros. On the Continent copper crushers are used.

The study of the pressures generated in fire-arms, together with determinations of the velocities of the projectiles, have rendered possible the

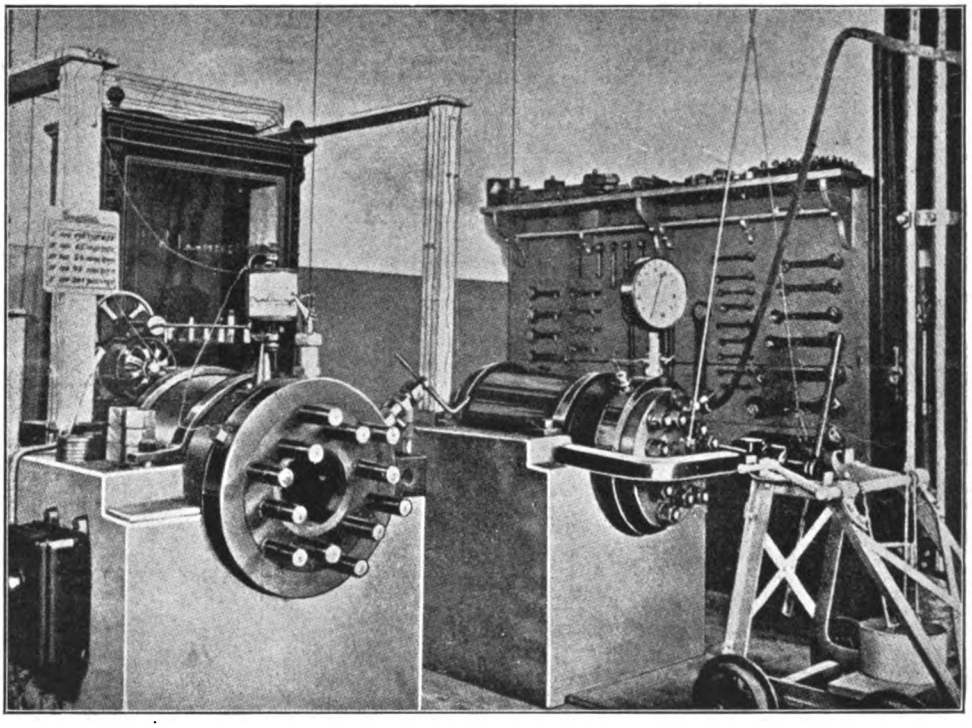

FIG. 84. Bichel's Recording Pressure Gauge

enormous advances in the construction of guns and in the manufacture of powders.

Recording pressure gauges.

The crusher gauge can, of course, be used in experiments in closed vessels, as was done by Noble and Abel (*see* Fig. 80), but it only shows the maximum pressure developed, and gives no indication of the time taken to reach this maximum, or the rate of increase in the different parts of the minute fraction of time occupied by the explosion. Various experimenters have therefore carried out tests in which the growth of the pressure was recorded automatically in much the same way as with a steam engine indicator. The pressure acts on a piston which is made to compress a spring and at the same time traces a mark on a drum, which is rotated very rapidly by means of an electric motor.

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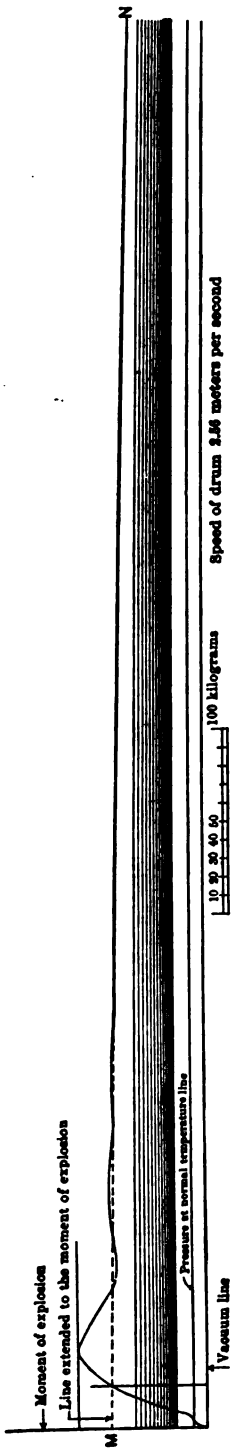

FIG. 85. Indicator Card from Bichel Pressure Gauge (from *Bureau of Mines Bulletin* No. 15)

Noble's.

Sir A. Noble in his experiments on cordite and other propulsive explosives[1] found it necessary, in order to record accurately the maximum pressures developed at high densities of charging, to screw down the spring beforehand, almost to the point corresponding to this maximum. Consequently, the part of the curve indicating the growth of the pressure could not be recorded.

Bichel's.

Bichel for investigating high explosives has used a bomb with a capacity of 15 litres (Fig. 84). In this a charge of 100 or 200 g. is exploded; consequently the density of charging is only 0·007 or 0·013. With black powder this gives a satisfactory diagram, but with high explosives the momentum acquired by the moving parts caused the maximum to be considerably too high, as may be seen in Fig. 85, but the true maximum may be ascertained by extending the line until it meets the normal corresponding to the moment of explosion. The curve gives some indication of the growth of the pressure but not a true measure of it. With such low densities the cooling effect of the walls of the bomb reduces the maximum pressure considerably. In order to eliminate this source of error Bichel uses two bombs of different sizes, and in the larger one he places one large or two small steel cylinders, so as to reduce the volume to 15 litres and at the same time increase the cooling surface. Three different areas are thus obtained with the same capacity. When the maximum pressures are plotted against these areas, the points lie almost on a straight line, and if this be continued until it cuts the normal corresponding to area nil, the theoretical pressure at this density is obtained.

Petavel's recording manometer.

Petavel in his recording manometer greatly diminished the vibration of the spring by making it much stiffer: the motion of the piston is then very small, but it is magnified many times by making it deflect a small mirror, which throws a beam of light on to a piece of sensitized paper wound on a drum, which is rotating rapidly.[2] The manometer is shown in

[1] *Discourse*, Royal Institution, 1900.

[2] *Phil. Trans.*, vol. 205, 1905, p. 357.

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Fig. 86. By means of the thread U the gauge screws into the explosion chamber, the end C of the piston being flush with the inside surface. An air-tight joint is formed by the ring D on the manometer pressing against a flat ledge. The end of the gauge from D to E is a good fit in the walls of the explosion chamber, and the joint is thus protected from the direct effect of the explosion. The spring S, about 5 in. in length, is tubular in shape. To prevent buckling it is made to fit the cylinder containing it at two places e_1 and e_2. At the outer end Z it is held by the nut K; at the inner end it is free to move and supports the piston P. As a gas check there is a leather

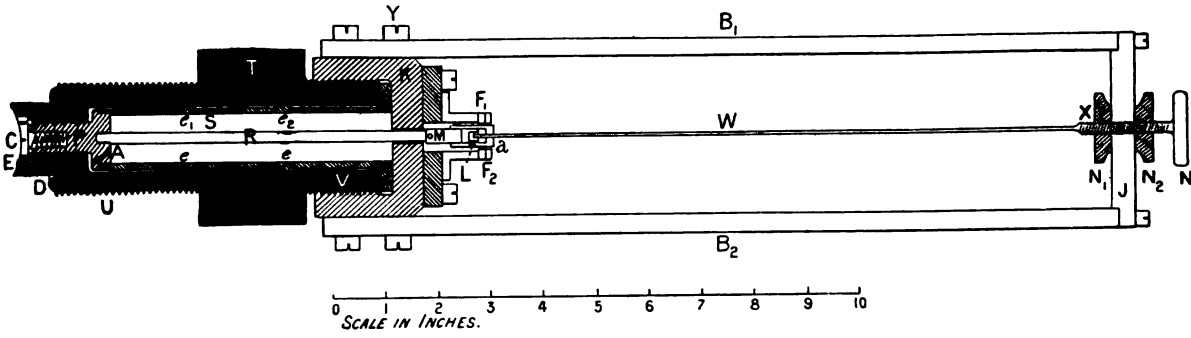

FIG. 86. Petavel's Recording Manometer

washer, which is attached to the piston by the screw C and to the fixed part of the gauge by the ring E. The end of the piston projects by about one-hundredth of an inch, and can therefore move back this distance without straining the leather. The motion of the piston is communicated by the rod R to a knife-edge (not shown) facing towards C. A lever is kept pressed against this knife edge by the tension in the wire W, which is stressed almost to its limit of elasticity. The lever is thus enabled to follow the motion of the piston, and by means of a small mirror it records it much magnified on the rotating drum. This recorder has given very satisfacfory results. Its time period is sufficiently small to allow records to be obtained not only of the curve of the rise of pressure of the smallest sizes of cordite, but also of the rapid vibrations which modify the curve under certain conditions (*see* Fig. 87, curve 4). It has not been applied, however, to the study of high explosives.

Relation of pressure to gravimetric density.

At medium temperatures and pressures their relation to one another and to the volume of a gas is represented very closely by the equation $pv = RT$, where p is the pressure, v the volume, T the temperature on the absolute scale, and R a constant. At high pressures it is necessary to introduce another constant and the equation becomes $p(v - b) = kT$. If we assume that the temperature of explosion remains constant at different densities of loading, this may be written $p(v - b) = c$. The constant b is called the co-volume and

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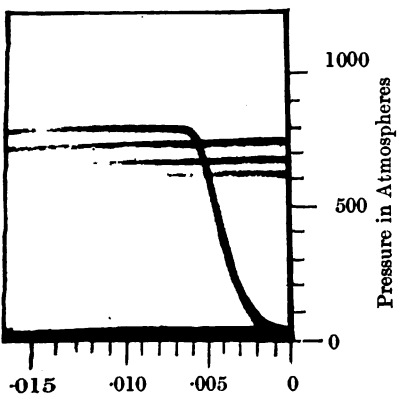
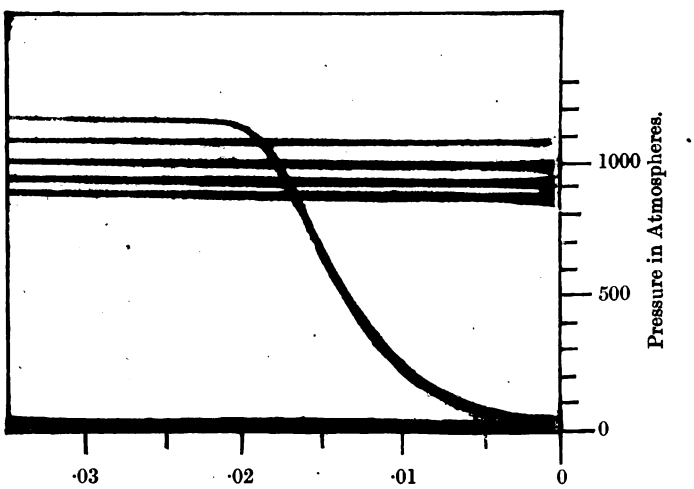
is supposed to represent the volume occupied by the actual substance of the molecules. In the case of cordite Mk.I, Petavel finds that the calculated pressures agree satisfactorily with those determined experimentally, if it be assumed that the co-volume is the same as the volume occupied by unit weight of solid cordite at the ordinary temperature, 0·641. At density 0·0744 he found a pressure of 5·137 tons per sq. in., hence

$$c = 5{\cdot}137\left(\frac{1}{0{\cdot}0744} - 0{\cdot}641\right) = 65{\cdot}75$$

Gravimetric density	Pressure calculated	Determined by Noble	Determined by Petavel
0·05	3·40	3·00	2·87
0·10	7·03	7·10	7·01
0·15	10·91	11·36	11·48
0·20	15·08	16·00	—
0·30	24·42	26·00	—
0·40	35·37	36·53	—
0·50	48·38	48·66	—
0·60	64·10	63·33	—



Curve 1.
Cordite, 0·035 inch diameter.
Gravimetric density, 0·0744.
Charge uniformly distributed in spherical enclosure.



Curve 3.
Cordite, 0·175 inch diameter.
Gravimetric density, 0·099.
Charge uniformly distributed in spherical enclosure.

FIG. 87. Curves from Petavel's Manometer

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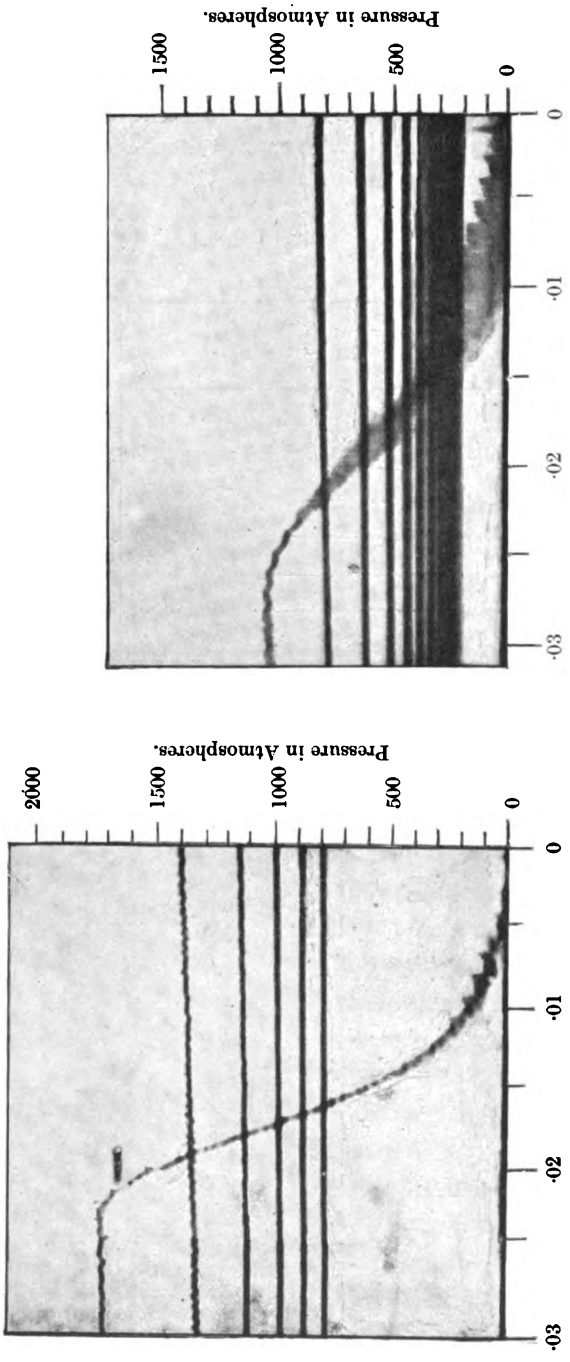

FIG. 87 (*continued*). Curves from Petavel's Manometer

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It is to be noted, however, that with this value for the co-volume, if the cordite were exploded in its own volume the equation gives an infinite pressure. It is clear, therefore, that with very high densities of loading a smaller value must be assumed for the co-volume.

If the temperature of explosion be known, and also the total volume of gas, it is possible to make a calculation of the pressure at any density, but more often the temperature is calculated from the pressure, as the latter can be determined directly, and the former cannot. In either case the calculations are unsatisfactory in consequence of the uncertainty as to the behaviour of gases at very high temperatures and pressures.

Calculation of Temperature

From the heat of explosion.

If the heat generated by the explosion be known, and also the nature and quantities of the products, it is possible to calculate their temperature at the moment of explosion, although it is somewhat doubtful whether the figure thus obtained really corresponds with what actually occurs. In order to make such a calculation it is necessary to know the specific heats of the products, that is, the quantity of heat required to raise the temperature of unit quantity through unit range of temperature. In such calculations it is most convenient to deal with molecular proportions of the products: if the percentage of each substance be divided by its molecular weight and multiplied by 10 it gives the number of "mols" per kg. of explosive. And if this be multiplied by the molecular specific heat it gives the quantity of heat required to raise the temperature of this constituent 1°. The specific heats, unfortunately, are not constant, but increase with rise of temperature, and there are considerable experimental difficulties in determining the specific heats of gases at very high temperatures. Mallard and Le Chatelier estimated them from the pressures generated by gaseous explosions in closed vessels,[1] and arrived at the following results:

Specific heats of gases.

Permanent gases: N_2, O_2, CO, H_2 . . .	$4{\cdot}80 + 0{\cdot}0006t$
CO_2, SO_2	$6{\cdot}26 + 0{\cdot}0037t$
Water vapour	$5{\cdot}61 + 0{\cdot}0033t$

These are mean molecular heats at constant volume: when multiplied by the temperature, t, they give the quantity of heat in small calories necessary to raise the temperature from 0° to t°. The total heat required to raise the temperature of the products to t° is given therefore by the equation

$$Q = At + Bt^2$$

A and B being obtained by multiplying the corresponding values of Mallard and Le Chatelier by the number of mols, adding them together and dividing

[1] *C.R.*, 1881, p. 1014.

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by 1000 to express the result in large calories. Solving the equation for t we have

$$t = \frac{-A + \sqrt{A^2 + 4BQ}}{2B}.$$

The above specific heats have been used by the French authorities for calculating the temperature of explosion of explosives for use in coal-mines: those for use in the coal seams must not give temperatures above 1500°, and those for the rock not above 1900°. Up to about 1500° these specific heats are probably fairly accurate, but there is considerable doubt as to the values for carbon dioxide and water vapour at higher temperatures. Similar explosion experiments were carried out by Langen,[1] who expressed his results by means of the formulæ:

Carbon dioxide	$6{\cdot}7 + {\cdot}0026t$
Water vapour	$5{\cdot}9 + {\cdot}00215t$

For the permanent gases his values are the same as those of Mallard and Le Chatelier.

More recently Pier has made explosion experiments in a spherical bomb with a capacity of 35 litres.[2] The pressure was measured by means of a corrugated steel diaphragm fixed in the side and carrying a mirror attached half way between the centre and the circumference. Results were obtained for temperatures from 1300° to 2500°. For lower temperatures up to 1400° values have been obtained by Holborn and Henning at constant pressure by the same method as was used by Regnault for determinations at temperatures up to a few hundred degrees, *i.e.* by passing the gas through a heated tube and then into a calorimeter. From these results and his own, Pier has calculated the following expressions for the mean molecular heats at constant volume between 0° and t°:

Monatomic gases (Argon) .	$2{\cdot}977$
Hydrogen . . .	$4{\cdot}700 + {\cdot}00045t$
Nitrogen, oxygen . .	$4{\cdot}900 + {\cdot}00045t$
CO_2, SO_2 . . .	$6{\cdot}800 + {\cdot}0033t - {\cdot}95t^2 \times 10^{-6} + {\cdot}1t^3 \times 10^{-9}$
Water vapour . . .	$6{\cdot}065 + {\cdot}0005t + {\cdot}2t^3 \times 10^{-9}$

Since 1907 gaseous explosions have been under investigation by a Committee of the British Association, which among other subjects has inquired into the specific heats. They maintain that there is an error in the determinations of Regnault and others at constant pressure due to over-correction for conduction of heat along the tube, through which the gases pass to the calorimeter. In consequence of this Regnault's results at moderate temperatures are 2 or 3 per cent. too low, and the error in those of Holborn and Henning is perhaps 7 per cent. Determinations have been carried out by Swann by a different method,

[1] *Mitteilungen über Forschungsarbeiten auf dem Gebiete des Ingenieurwesens*, Heft 8, 1903.
[2] *Zeits. Elektroch.*, 1909, p. 536; 1910, p. 897.

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the gas being heated by means of an electric coil, and the rise of temperature being measured as well as the energy supplied.[1] He thus obtained for air a value of 5·00 at 20°, which is near that calculated from Joly's determination, with a steam calorimeter, which gave 4·96, whereas Regnault's figure was 4·86 and Wiedemann's and Witkowski's were practically the same. For carbon dioxide Swann got 6·93 at 20° and 7·76 at 100°, which again is substantially higher than the older figures. Dugald Clerk has carried out experiments with air in an engine cylinder, and has calculated the specific heat from the curve on the indicator diagram: the mean specific heat between 20° and 120° is calculated to be 5·23. Hopkinson has made similar experiments, in which, however, he has also measured the temperature directly, and has arrived at the value 5·23 over the range 20° to 270°. With gas-engine mixture at a temperature of 1400°, Clerk obtained results in agreement with the specific heats of Langen. Those of Holborn and Henning would be about 8 per cent. lower, and those of Mallard and Le Chatelier several per cent. higher.

The question of specific heats has also been investigated from the purely theoretical standpoint. By means of Planck's Quanten Theory it is possible to calculate from the spectrum of the gas the variation of the specific heat with the temperature. It can thus be shown that the general form of Pier's expression for carbon dioxide is correct, that is to say the specific heat increases rapidly up to about 1000° and then more slowly. In the case of water vapour the increase continues to accelerate up to a very high temperature. Nernst has done much to develop this theory.[2]

The net result is that up to a temperature of about 1500° the specific heats are known approximately; but above this they are still very uncertain, and temperatures of explosion calculated from the heat liberated are of little value. The uncertainty is rendered still greater by an observation of Pier, who attempted to measure the equilibrium of the reaction $CO_2 + H_2 = CO + H_2O$. The results were quite unsatisfactory, and he has suggested that this may have been due to the formation of an endothermic compound of carbon dioxide and water at a high temperature. There is also some uncertainty as to the effect of high temperature combined with high pressure on the specific heats of water vapour and carbon dioxide. Both these substances are liable to dissociate at high temperatures, but to what extent is not known; the amount of dissociation would be diminished by high pressure.

Specific heats of solids.

There is also some uncertainty about the specific heats at high temperatures of the solid products of explosion. Approximately they follow at ordinary temperatures the law of Kopp: that is to say, the molecular heat of the compound is equal to the sum of the atomic heats of the elements composing it, and the latter, in accordance with the law of Dulong and Petit, mostly have a value of about 6·4. The following have lower values, however: C 1·8,

[1] *Proc. R.S.*, 1909, A., p. 147.

[2] *See also* Bjerrum, *Zeits. Elektroch.*, 1912, p. 101.

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H 2·3, Si 3·8, O 4·0, P and S 5·4. With rise of temperature there always is an increase in the specific heats, but at very high temperatures the rate of increase diminishes. Those elements and compounds, which have low atomic heats at the ordinary temperature, show greater increases with temperature. All the atomic heats seem to approach a constant value of 7 or 8 at high temperatures. For the temperatures concerned in explosive reactions approximately accurate results are probably obtained by assuming that the mean specific heat between 0° and t° increases by 0·0002 of its value at the ordinary temperature for every degree. Thus if S_0 be the specific heat at the ordinary temperature the mean specific heat is $S_0(1 + 0{\cdot}0002t)$.

Products of explosion.

The specific heats of many of the substances that are liable to occur among the products of explosion are given in App. II, pp. 602–604.

If an explosive contain more oxygen than is sufficient to oxidise all the hydrogen to water and the carbon to dioxide, it gives practically the same result in the bomb calorimeter whatever the density of loading, provided that due allowance be made for the detonator or other means of ignition : [1] the heat evolved is the same, as also are the volume and the composition of the gases.

If the explosive do not contain sufficient oxygen for the complete combustion of the hydrogen and carbon, differences are observed when the density is varied : with increase of the density of loading the reis considerable increase in the quantity of heat liberated, and a diminution in the total volume of gas. As regards the separate products of explosion, there is a considerable increase in the amount of CO_2 and CH_4, and a diminution in the CO and H_2, and a lesser one in the water.

It is argued by Poppenberg and Stephan [2] that at the moment of explosion the composition of the products is the same, whatever the density of loading, and consequently the heat of explosion is also the same. The differences found are ascribed to reactions taking place during the cooling of the products. When the density is high, there is a larger quantity of heat to be conducted away through the same cooling surface, consequently the time of cooling is longer, and the secondary reactions proceed further. There is no doubt much truth in this contention : it may not be strictly accurate in the case of propulsive explosives, because with them the time of explosion is comparatively long, and secondary reactions must take place in some portion of the products before the whole of the powder is consumed. With detonating explosives the course of the change is no doubt different, but from the study of the explosion of gaseous mixtures there is reason to think that the products formed in the wave of detonation are not necessarily those which are most stable at the temperature of explosion. The change takes place therefore in three stages : first, certain products are

[1] *See S.S.*, 1907, p. 306.

[2] *S.S.*, 1909, pp. 281, 305 ; and 1909, p. 388 ; 1910, pp. 266, 291, 310, 452, 474. *See also* Kast, *S.S.*, 1910, pp. 205, 248, 376, 399.

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formed in the detonation wave, then almost instantaneously other reactions take place so that an equilibrium is set up corresponding to the temperature of explosion : at this very high temperature the reactions proceed with enormous velocity. Finally, as the temperature falls the composition corresponding to stable equilibrium gradually changes : at first the composition of the gases follows very closely the equilibrium composition, but as the temperature gets lower, it lags behind more and more until the velocity of change becomes negligible.

One of the reactions that takes place as the temperature falls is :

$$CO + H_2O = CO_2 + H_2 + 10{\cdot}1 \text{ Cals. (water, gas)}.$$

If the water be liquid, there is instead a negative production of heat of $-0{\cdot}4$ cals., so that the actual thermometer reading in the calorimeter is practically unaffected and, even when the result has been corrected for the condensation of water, the effect is not great. The total volume of gas is also unaffected by the reaction, as there are two molecules on each side of it. The reaction is not a complete one, but tends towards an equilibrium, which shifts with the temperature. At any temperature the relation $(CO)(H_2O)/(CO_2)(H_2) = k$ is constant, whatever the actual quantities of the different gases. From various thermo-dynamical data, Haber [1] has calculated that the relation of k to the absolute temperature is given by the equation :

$$\log k = -2116/T + 0{\cdot}783 \log T - 0{\cdot}00043\, T$$

the logarithms being common ones. The equation has been confirmed by experiments with gas flames. If $T = 2000°$ $k = 4.61$, and if $T = 3000°$ $k = 5{\cdot}31$. Poppenberg and Stephan prefer, however, to take $k = 7$ about, for the temperature of explosion, this figure being deduced from calculations by Langen and others. But this difference only diminishes the calculated heat of explosion by quite a few calories.

Formation of methane.

A reaction that affects the results considerably more is the formation of methane. Poppenberg and Stephan consider that no methane exists at the moment of explosion, but that it is formed, as the gases cool down, by the action of the hydrogen on the oxides of carbon, or on carbon itself if there be any present. In support of this view they have shown experimentally that if powder gases be kept in contact with a Nernst light, a considerable percentage of methane is formed. If picric acid or trinitro-toluene be detonated in a bomb in the ordinary way there is much methane, especially at high densities of loading, but if they be detonated in their own volume in a small block placed inside a bomb, there is not more than 0·5 per cent. Under these circumstances the gases are cooled very rapidly in consequence of the work done in destroying the block, and no time is afforded for the formation of methane. Moreover it

[1] Thermodynamik der technischen Gasreaktionen.

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has been shown by Mayer and Altmayer [1] that methane cannot exist at a very high temperature. The formation of methane is represented by the equations :

$$CO + 3H_2 = CH_4 + H_2O + 50{\cdot}7 \text{ Cals.}$$
$$CO_2 + 4H_2 = CH_4 + 2H_2O + 40{\cdot}6 \text{ Cals.}$$

However it may be produced, for every volume of methane the total volume of gas is reduced by two volumes, and the heat is increased. With an increase in the proportion of hydrogen the formation of methane is greatly accelerated : the formation is proportional to the cube or the fourth power of the concentration of the hydrogen. Hence trinitro-toluene, which gives much hydrogen on detonation, is liable to give also much methane.

Of ammonia. The same conditions also favour the formation of ammonia $2NO + 5H_2 = 2H_2O + 2NH_3$ whereas if there be only a moderate amount of hydrogen, the reaction is mostly in accordance with the equation $2NO + 2H_2 = 2H_2O + N_2$. Poppenberg and Stephan found considerable quantities of ammonia when trinitro-toluene and dinitro-benzene were detonated in their own volume and made to do work, so apparently it is formed at a high temperature.

Carbonates. If the explosion produce a solid residue, further complications are introduced. Metallic oxides are generally converted into carbonates and bicarbonates, and in making the calculations it is necessary, therefore, to allow for the

Carbon. carbon dioxide thus combined, and for the heat produced. Some explosives leave a residue of carbon. Thus Poppenberg and Stephan [2] found that picric acid, detonated in a lead block inside a bomb, gave 6 per cent. of carbon. The amount, however, depends on the violence of the detonation, for if a very powerful primer be used there is much carbon. But if the gases cool gradually in contact with the carbon, the latter is acted on by the water vapour, as in the production of water gas : $C + H_2O = CO + H_2 - 28{\cdot}3$ Cals. The temperature is reduced by this reaction and the volume of gas increased. It was found that according to the circumstances the following percentages of carbon could be recovered from the residues of detonation :

	In lead block (Doing work)	In bomb $\Delta = {\cdot}02$
Picric acid	6·0 per cent.	0·29 per cent.
Trinitro-toluene . . .	17·2 ,,	4·82 ,,
Dinitro-benzene . . .	19·37 ,,	—

At higher densities detonation in the bomb would have given still lower percentages.

Aluminium. The effect of aluminium is somewhat similar, it is added generally in the form of a fairly coarse powder, partly in order to retard its oxidation during storage. It cannot take part very largely in the original explosive reaction

[1] *B.*, 40, 1907, p. 2134.

[2] *S.S.*, 1910, p. 294.

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but afterwards it reduces the water and carbon dioxide with the production of much heat :

$$2Al + 3CO_2 = Al_2O_3 + 3CO + 176{\cdot}4 \text{ Cals.}$$
$$2Al + 3H_2O = Al_2O_3 + 3H_2 + 206{\cdot}5 \text{ Cals.}$$

When ammonal was detonated in a porcelain block, Poppenberg and Stephan found that a considerable proportion of the aluminium remained unoxidized. There was also 3·36 per cent. of methane in the gases and 2·62 per cent. of other hydrocarbons, mostly acetylene, whereas when the ammonal was exploded in a bomb in the usual way at a density of 0·02, the percentage of acetylene was only 0·2 to 0·6 per cent. They consider that in this case, as also in that of dinitro-benzene, the methane is not formed directly, but acetylene is first produced from carbon monoxide and hydrogen at a high temperature :

$$2CO + 3H_2 = HC : CH + 2H_2O$$

and the methane is formed from this.

Calculation of temperature from pressure.

At moderate pressures the relationship between the volume, temperature and pressure of a given quantity of gas is represented with sufficient accuracy by the equation

$$p_1v_1/T_1 = p_2v_2/T_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or by

$$pv = (t + 273)/273 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where v is the volume occupied at $t°$ and under a pressure of p atmospheres by a quantity of gas, which at 0° and 1 atmosphere has a volume of 1. At high pressures there are considerable divergences from this formula, however, especially in the neighbourhood of the critical temperature. The behaviour of gases is better represented by the equation of van der Waals

$$(p + a/v^2)(v - b) = (t + 273)/273 \quad . \quad . \quad . \quad . \quad (3)$$

a and b being constants, varying with each gas, which can be calculated from the critical temperature and pressure. Temperatures of explosion are much higher than the critical temperatures, and it is found that the application of the corrections in equation (3) makes but little difference at pressures of about 1000 atmospheres and temperatures of 1000° to 2000°, and in view of the many uncertainties attaching to these calculations it is not worth while applying this equation : it is better to adhere to the simpler forms (1) and (2).

At pressures above about 1500 atmospheres the relationship alters somewhat : the term a in van der Waal's equation, which represents the attraction between the molecules brought into play by the diminution of the volume, disappears. The term b, which represents the co-volume, or volume actually occupied by the molecules, remains, but assumes a value somewhat smaller than that calculated from the critical data. The variation with temperature also alters. The behaviour of various gases at pressures ranging from 100 to 1000 atmo-

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spheres and temperatures from 0° to 200° was investigated by Amagat ; and at the ordinary temperature he extended the observations to 3000 atmospheres. The results of his experiments, between 500 and 2000 atmospheres pressure, are represented fairly well by an equation of the form

$$p(v - b) = (t - t_k)/C \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where t_k is the critical temperature of the gas and C is a constant. The following Table gives the values of these terms for the principal gases concerned :

Substance	Critical temperature	From critical data		From high pressure measurements	
	t_k	a	b	b	C
Nitrogen	− 146°	·0027	·0017	·0013	220
Oxygen	− 118°	·0027	·0014	·0011	220
Hydrogen . . .	− 242°	·0004	·0009	·0007	260
Carbon dioxide . .	+ 31°	·0070	·0018	·0012	150
Carbon monoxide .	− 140°	·0028	·0017	·0012	260
Methane	− 90°	·0037	·0016	·0009	150
Water vapour . . .	+ 360°	·0117	·0015	(·001)	(150)

In the case of water there are no direct measurements available at high pressures and at temperatures well above the critical point, so that the values of b and C can only be estimated by analogy.

At pressures above 2000 atmospheres the co-volume b further decreases, and the equation should apparently be written in the form

$$p(v - b) + p^2c = (t - t_k)/C \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

in which c has a value of about 5×10^{-8} but the data available are not sufficient to establish the relationship with certainty in the region of these very high pressures.

In calculations of this kind it is sometimes assumed that the co-volume b has a uniform value of 0·001 of the volume of gas at 0° and 1 atmosphere. Noble and Abel assigned to it for cordite a value of 0·65 or 0·60 of the weight of the explosive in grammes, and as this explosive produces about 890 c.c. per gramme, these figures correspond to a co-volume of 0·00073 or 0·00067 of the volume of gas. But Noble and Abel's pressure results are not corrected for the cooling effect of the walls of the vessel, although they recognized the existence of this source of error.

Direct measurement of temperature.

Macnab and Ristori proposed to measure the temperatures generated by propellent explosives by the use of a series of thermocouples of various thicknesses. From the results they intended to estimate what current would be

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obtained, if the wires of the thermocouples were of negligible thickness, and hence to calculate the temperatures.[1] The temperatures might perhaps be measured by means of an optical pyrometer in much the same manner as was done by Borland in the case of percussion caps (*see* p. 428).

Examples of Calculations

Hall and Howell [2] have made some experiments with an explosive having the following composition :

Component	Formula	Per cent.	Molecular weight	Mols per kg.	Heat of formation		Ultimate composition Gramme-atoms			
					Molecular	Total	C	O	N	H
Ammonium nitrate	$N_2H_4O_3$	89·08	80·1	11·12	88·05	979·2	—	33·36	22·24	44·48
Trinitro-toluene .	$C_7H_5N_3O_6$	6·57	227·2	0·29	10	2·9	2·06	1·74	·87	1·45
Nitro-naphthalene	$C_{10}H_7NO_2$	4·19	173·1	0·24	−13·8	−3·2	2·42	·48	·24	1·70
Moisture . .	H_2O	0·17	18·0	0·09	68·4	6·4	—	·09	—	·18
		100				985·3	4·48	35·67	23·35	47·81

Of this, 100 grammes were fired in a Bichel calorimeter by means of a No. 7 detonator. In three experiments the number of Calories found per kg. after

Product	Per cent.	Molecular weight	(2) × (3)	Mols per kg.	Heat of formation		Ultimate composition Gramme-atoms			
	(2)	(3)	(4)	(2) $\frac{559·5}{3239}$	Molecular	Total	C	O	N	H
CO_2	26·7	44·0	1173	4·610	97·0	447·2	4·61	9·22	—	—
O_2	3·2	32·0	102	·553	—	—	—	1·11	—	—
N_2	70·1	28·0	1964	12·105	—	—	—	—	24·21	—
	100		3239	17·268						
Gases	55·95									
H_2O	43·03	18·0		23·90	68·4	1634·8	—	23·90	—	47·80
O (as SnO_2) . .	1·02	16·0	(SnO_2	·32)	141	45·1	—	·64	—	—
	100			41·17		2127·1	4·61	34·87	24·21	47·80
						985·3				
						1141·8				
Correction to constant volume, 17·3 × 0·58						10·0				
						1151·8				

[1] *Proc. Roy. Soc.*, 66, p. 221.

[2] *Bureau of Mines Bulletin* 15.

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deducting 8·6 Cals. for the detonator were 1208, 1211, and 1171, mean 1197. Two hundred grammes wrapped in 7·6 grammes of tin foil were also fired in a Bichel pressure gauge. The products of explosion were found to consist of 111·9 grammes of gas having the composition given below and 84·2 grammes of water. Of the loss it may be assumed that 2·04 grammes of oxygen were consumed in converting the tin foil into oxide of tin, and the remaining 1·86 grammes were water. Then we have for the products of explosion (*see* Table at bottom of page 377). The heat calculated from the analyses, 1152 Calories, is somewhat less than that found. The agreement in the elementary composition is not very good either. If now the heat be calculated from the analysis of the explosive on the assumption that part of the defective oxygen has been consumed in converting the tin foil into tin oxide and the remainder of it has formed a thin layer of iron oxide in the interior of the bomb, we have for the products :

Product	Mols per kg.	Heat of formation	Calories
CO_2	4·48	97·0	434·6
O_2, N_2	12·23	—	—
H_2O	23·90	68·4	1634·8
SnO_2	·32	141·0	45·1
Fe_3O_4	·25	271·0	67·7
			2182·2
			985·3
			1196·9 + 10·0 = 1206·9

It is noticeable that the third determination of the heat of explosion gave results considerably below the first two. This may have been due to the formation of a protective coat of oxide on the surface of the steel. Eliminating the third result, the mean of the other two is 1209·5, agreeing well with the above. As the gaseous products of the detonator are not included in this calculation, no allowance is to be made on this account.

In calculating the temperature of explosion in the pressure bomb it is necessary to take into account the products of the detonator. To 200 grammes of explosive there are 1·275 g. fulminate of mercury, 0·225 of chlorate of potassium and about 3 g. of metallic copper. The following Table gives the number of mols per kg. of the various solid products and the molecular specific heats at the ordinary temperature :

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Product	Mols per kg.	Molecular Specific Heat	Calories
SnO_2	0·32	14·0	4·48
Cu	0·24	5·8	1·39
Hg	0·02	6·6	·13
KCl	0·01	12·6	·13
Fe_3O_4	0·25	36·5	9·12
			15·25

Strictly speaking, the mercury should be considered as vapour, but the amount is so small, that it is not worth while making the necessary additional calculations, but if only a few grammes of explosive be used, this correction should be made. The detonator also produces 0·045 mol of CO_2 and 0·022 of N_2 but requires 0·009 mol of O_2 to complete the oxidation of the carbon. Hence we have, using Mallard and Le Chatelier's specific heats :

Product	Mols per kg.	Molecular heat	Calories per °C.
CO_2	4·52	$6·26 + ·0037t$	$28·29 + ·0168t$
O_2, N_2	12·24	$4·80 + ·0006t$	$58·75 + ·0073t$
H_2O	23·90	$5·61 + ·0033t$	$134·08 + ·0789t$
Solids	—	$15·25 + (1·0002t)$	$15·25 + ·0030t$
	40·66		$236·37 + ·1060t$

The heat of explosion requires to be corrected for the heat of condensation of the water vapour, and the heat due to the detonator must be added on again, but only half the amount, as twice as much explosive was used in the pressure bomb :

$$1197 - 23·9 \times 10·4 + 4·3 = 952·7 \text{ Cals.}$$

$$t = \frac{-·2364 + \sqrt{(·2364^2 + 4 \times ·000106 \times 953)}}{2 \times ·000106} = 2037°$$

Using Pier's specific heats we have :

CO_2	$4·52(6·800 + ·0033t - ·95t^2 \times 10^{-6} + ·1t^3 \times 10^{-9})$
N_2, O_2	$12·24(4·900 + ·00045t)$
H_2O	$23·90(6·065 + ·0005t - ·2t^2 \times 10^{-6} + ·2t^3 \times 10^{-9})$
Solids	$15·25(1 + ·0002t)$
Total	$250·9 + ·0246t - 4·29t^2 \times 10^{-6} + 5·23t^3 \times 10^{-9}$

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Assuming a temperature of 2600°, this gives $t = 2521°$. Assuming next a temperature of 2550°, we get $t = 2560°$, which may be taken as the temperature by this method.

From pressure. The following pressures were recorded with Bichel gauges arranged with different cooling surfaces, the charge being 200 grammes and the volume of the gauges 15 litres :

Cooling surface	Pressure at time 0 from indicator card Kilogrammes per sq. cm.			Mean
3914 sq. cm.	110·63	107·50	105·63	107·92
6555 ,,	100·00	100·00	98·75	99·58
7624 ,,	95·63	95·00	98·75	96·46

Hence it is calculated that with no cooling surface the pressure would be 119·92 kg./cm.^{2} equal to 116·0 atmospheres. The volume of gas at 0° and 1 atmosphere is given by the number of mols. of gas multiplied by 22·41. Hence we have :

$$T = \frac{116 \times 15 \times 273}{40{\cdot}66 \times 22{\cdot}41 \times 0{\cdot}2} = 2606$$

$$t = 2606 - 273 = 2333°$$

The agreement with the temperature as calculated with Pier's specific heats is not satisfactory, although these are based on the pressures developed by the explosion of gas mixtures and recorded by a gauge somewhat similar to that of Bichel. The fault may lie partly with the Bichel gauge, the moving parts of which are heavy, and not sufficiently rigid, with the result that the pencil oscillates violently during the first hundredth of a second (*see* Fig. 85). The pressure at the moment of explosion has been deduced from the subsequent pressures on the assumption that the rate of cooling is uniform : but this is not the case, for the surfaces are originally cold and take up heat at first much more rapidly than they do when they have become warm. An inspection of Petavel's results shows that the early part of the pressure curve resembles a parabola more than a straight line. It is possible, therefore, that the pressures have been under-estimated somewhat. Another cause for the discrepancy is the anomalous behaviour of mixtures of water vapour and carbon dioxide at high temperatures, possibly due to the formation of an endothermic compound. The true temperature of explosion is possibly somewhere between2350° and 2550°.

If the explosive contain alkali nitrates, it is necessary to take into account the formation of bicarbonates, and if the oxygen be insufficient for complete oxidation, other complications are introduced. Another explosive examined by Hall and Howell had the composition :

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Component	Formula	Per cent.	Molecular weight	Mols. per kg.	Heat of formation		Ultimate composition Gramme-atoms			
					Molecular	Total	C	O	H	N
Nitro-glycerine	$C_3H_5N_3O_9$	24·92	227	1·098	94·2	103·4	3·29	9·88	5·49	3·29
Saltpetre	KNO_3	25·37	101	2·512	119	298·9	—	7·54	—	2·51
Barium nitrate	BaN_2O_6	4·42	261	·169	227·2	38·4	—	1·01	—	·34
Wood-meal	$C_{50}H_{72}O_{33}$	34·60	1200	·288	1500	432·4	14·41	9·51	20·76	—
Starch	$C_6H_{10}O_5$	6·64	162	·410	225·9	92·6	2·46	2·05	4·10	—
Moisture	H_2O	4·05	18	2·250	69·0	155·2	—	2·25	4·50	—
		100				1120·9	20·16	32·24	32.85	6·14
Products of detonator							·08	·14	—	·08
							20·24	32·38	34·85	6·22

In the pressure bomb 200 grammes fired with a No. 7 detonator gave 130·3 g. of gas, 37·3 g. of soluble solid (potassium bicarbonate), 11·7 g. of insoluble solid (barium carbonate) and 12·4 g. of water. The loss was therefore 8·3 g., or allowing for the non-metallic products of the detonator 8·76 g. The figures for the solid products do not agree at all with the analysis of the explosive, which would give 50·24 g. of potassium bicarbonate and 6·72 of barium carbonate. Assuming that the latter figures are the more correct, and that a little water was lost as well as a portion of the solids, we have :

Product	Per cent. by volume	Molecular weight	Proportions by weight	Mols. per kg.	Heat of formation		Ultimate composition Gramme-atoms			
					Molecular	Total	C	O	H	N
CO_2	18·9	44	832	5·41	94·3	510·2	5·41	10·82	—	—
CO	36·3	28	1016	10·39	26·1	271·2	10·39	10·39	—	—
H_2	29·1	2	58	8·33	—	—	—	—	16·66	—
CH_4	5·8	16	93	1·66	18·6	30·9	1·66	—	6·64	—
N_2	9·9	28	277	2·83	—	—	—	—	—	5·66
	100		2276	28·62						
Gases	65·15									
$KHCO_3$	25·12	100	—	2·51	233·3	586·0	2·51	7·54	2·51	—
$BaCO_3$	3·36	197	—	·17	282·5	47·7	·17	·51	—	—
H_2O	6·83	18	—	3·80	69·0	362·2	—	3·80	7·60	—
	100·46					1708·2	20·14	33·06	33·41	5·66
						1120·9				
						587·3				

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To this must be added 28·62 × 0·58 Cals. to correct to constant volume, and about 1·2 Cals. are to be subtracted for the partial solution of the potassium bicarbonate, which brings the result to 602·7 Cals.

The heat of explosion as determined directly in the calorimetric bomb was in three experiments: 575, 567 and 570 Calories, mean 570·7, to which must be re-added 4·3 for the detonator, making it 575, as compared with 602·7 Calories by calculation from the analyses. Berthelot's heats of formation have been used in the calculations.

In calculating the state of the products at the moment of explosion it is necessary to convert all the potassium bicarbonate to carbonate and the liquid water into vapour. The former change proceeds in accordance with the equation: $2KHCO_3 = K_2CO_3 + CO_2 + H_2O - 35{\cdot}4$ Cals. (water gas), and the vaporization of the water at 18° absorbs 10·5 cals. according to Winklemann's formula. On the other hand 1·2 cals. are to be added on account of the bicarbonate being no longer in solution: $575 - 17{\cdot}7 \times 2{\cdot}51 - 3{\cdot}80 \times 10{\cdot}5 + 1{\cdot}2 = 491{\cdot}9$ Cals. By the reconversion of the methane the available heat is further reduced: $CH_4 + H_2O = CO + 3H_2 - 50{\cdot}7$ Cals., $491{\cdot}9 - 1{\cdot}66 \times 50{\cdot}7 = 407{\cdot}7$ Cals. The total number of mols of gas after making these corrections is 38·26.

The pressure generated by 200 grammes in a 15-litre bomb corrected for surface cooling was 67·0 kg./cm.² equal to 64·85 atmospheres. Hence the temperature as calculated from the pressure is

$$T = \frac{64{\cdot}9 \times 15 \times 273}{38{\cdot}26 \times 22{\cdot}41 \times 0{\cdot}2} = 1549$$

$$t = 1276°$$

At this temperature the equilibrium constant $k = (CO)(H_2O)/(CO_2)(H_2) = 2{\cdot}8$, and it is necessary to adjust the quantities of the different gases accordingly. These various changes are shown in the following Table:

Product	Original Analysis	Correction for		Result	Corrected to $k = 2{\cdot}8$
		Bicarbonate	Methane		
CO_2	5·41	+ 1·26	—	6·67	3·51
CO	10·39	—	+ 1·66	12·05	15·21
H_2	8·33	—	+ 4·98	13·31	10·15
H_2O	3·80	+ 1·26	− 1·66	3·40	6·56
N_2	2·83	—	—	2·83	2·83
CH_4	1·66	—	− 1·66	—	—
$KHCO_3$	2·51	− 2·51	—	—	—
K_2CO_3	—	+ 1·26	—	1·26	1·26
$BaCO_3$	·17	—	—	·17	·17

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The last change involving 3·16 mols. of each of the gases reduces the heat available by 3·16 × 10·1 cals., and brings it to 375·8 cals. The calculation of the temperature with Mallard and Le Chatelier's specific heats is as follows :

	Mols.	Specific Heat	
Solids			
K_2CO_3 . . .	1·26 × 28·4 =	35·78	
$BaCO_3$ . . .	·17 × 21·8 =	3·71	
Sn	·32 × 6·5 =	2·08	
Cu . . .	·24 × 5·8 =	1·39	
Hg . . .	·02 × 6·6 =	·13	
KCl . . .	·01 × 12·6 =	·13	
		43·22 × (1 + ·0002t) =	43·2 + ·0086t
Gases			
CO, H_2, N_2		28·19 × (4·80 + ·0006t) =	135·3 + ·0169t
CO_2		3·51 × (6·26 + ·0037t) =	22·0 + ·0130t
H_2O		6·56 × (5·61 + ·0033t) =	36·8 + ·0216t
			237·3 + ·0601t

Hence it is calculated t = 1222°.

The agreement is not very close : Mallard and Le Chatelier's specific heats may be somewhat too high even at this comparatively low temperature. On the other hand, there may have been some formation of methane before the pressure gauge registered. Over-correction for methane would reduce the temperature as calculated from the pressure, but would reduce that calculated from the heat about four times as much. The actual maximum temperature attained in the bomb may be estimated roughly at 1300°.

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CHAPTER XXVIII

POWER AND VIOLENCE OF EXPLOSION

Power of explosives : Trauzl test : Ballistic pendulum : The time factor : Mettegang recorder : Dautriche's method : Velocity of sound : Influence of density : Influence of diameter : Of envelope : Of primer : Of temperature : Velocity of detonation of nitro-glycerine : Of nitro-glycerine explosives : Of sundry explosives : Brisance : Tests under water

Power of explosives.

In the last chapter methods were dealt with for the determination and calculation of the temperature, pressure and volume of the products of explosion. These three quantities are interdependent, so that if we know two of them, we should be able to calculate the third; we could do this with certainty if we were better acquainted with the behaviour of the products at these high temperatures and pressures. If the explosion take place at a fairly low density, the relationship is given by the equation: $PV/T = V_0/273$, where P is the pressure of explosion in atmospheres and T is its absolute temperature, V is the volume of the vessel in which the explosion takes place, and V_0 is the volume of the products calculated at 0° C. and 1 atmosphere pressure. The potential energy of the gases is

$$PV = \frac{V_0 T}{273} = \frac{V_0 Q}{273\,c}$$

where Q is the quantity of heat liberated in the explosion, and c is the mean specific heat of the products, a very uncertain quantity. Berthelot has given to the expression V_0Q/c the name of "characteristic product,"[1] and used it as a measure of the power of the explosive. But in consequence of the difficulty of ascertaining the value of c, the product V_0Q has often been used instead. It is preferable, however, both on theoretical and practical grounds to use the other side of the above equation, and measure the strength of the explosive by the product PV. It is true that V_0 and Q can be measured or calculated without any great difficulty, but they require to be corrected for various changes that take place during the cooling of the gases, and the exact magnitude of the corrections is by no means certain. On the other hand, P

[1] Produit caractéristique, *see Force des Matières explosives*, vol. i, p. 64; *Explosives and their Power*, p. 32.

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can be determined in a pressure gauge, such as that of Bichel, and only requires to be corrected for the cooling action of the surface, and the measurements in the instrument itself supply this correction. V, the volume of the gauge, is of course easy to ascertain and is constant. For one and the same instrument and weight of charge the power of the explosive may be taken as proportional to the pressure developed.

In a series of experiments carried out by Bichel in 1902 [1] the pressures found were nearly proportional to the results obtained in the Trauzl lead block, but the product V_0Q did not show the same degree of regularity :

	V_0 Lit./kg.	Q Cal./kg.	$\frac{V_0Q}{1000}$	P	Trauzl Test
Blasting gelatine	851	1422	1210	70·4	650
Gelignite 65 per cent.	487	1321	643	55·4	560
Dynamite No. 1	536	1170	627	48·2	520
Donarite	1023	836	856	48·7	500
Ammon-carbonit I.	922	850	782	46·8	470
Ammon-carbonit	930	757	703	42·2	330
Thunderite	1021	777	794	38·0	310
Carbonit II	746	602	448	34·7	300
Carbonit I.	773	601	464	32·4	290
Kohlen-carbonit	816	506	412	31·0	270
Carbonite	729	576	420	26·6	265
Gunpowder	386	574	228	18·7	108

The pressures are in kilogrammes per square centimetre developed by 100 g. in a 15-litre chamber after elimination of the surface influence. Bichel obtained no result with gunpowder in the lead block, using ordinary stemming : the value given above was obtained by Tschokke, who stemmed it with Portland cement.

Trauzl's lead block test affords a ready means of ascertaining the approxi- **Trauzl test.** mate relative strength of explosives. It consists in firing a charge of the explosive in a hole in a block of lead and measuring the size of the cavity formed. At the Fifth International Congress of Applied Chemistry, held at Berlin in 1903, standard conditions were laid down for carrying out the test :

" *The lead cylinder* is 200 mm. in height and 200 mm. in diameter. In its axis is a hole 125 mm. deep and 25 mm. in diameter to take the charge. The purest refined soft lead should be used, and for comparative trials the cylinders should all be from one melting. The sketch (Fig. 88) shows a convenient form of mould for casting the blocks. In order to pre-heat the mould, a red-hot ring is placed round it.

[1] *Testing Explosives*, Table I.

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"*The Process.* The blocks should be allowed to stand after casting sufficiently long to attain a uniform temperature of 15° to 20°. Ten g. of the explosive are weighed out and wrapped in a piece of tin-foil, of 80 to 100 g. per sq. metre, of the dimensions shown at the bottom of Fig. 88, so as to form a cartridge of 25 mm. diameter. An electric detonator containing a charge of 2 g. is inserted into the centre of the cartridge. The cartridge is carefully pressed home with a wooden rod keeping the wires central. For tamping, sharp dry quartz sand is used, which passes through a sieve of 144 meshes per sq. cm. (30 meshes to the inch), the wire being 0·35 mm. thick. The sand is run in until the hole is full, and the excess is removed. The charge is then fired electrically. Afterwards the lead block is inverted and any residue is removed with a brush. The quantity of water is then ascertained that is required exactly to fill the cavity. This, less the original volume of the hole, gives a measure of the power of the explosive.[1]

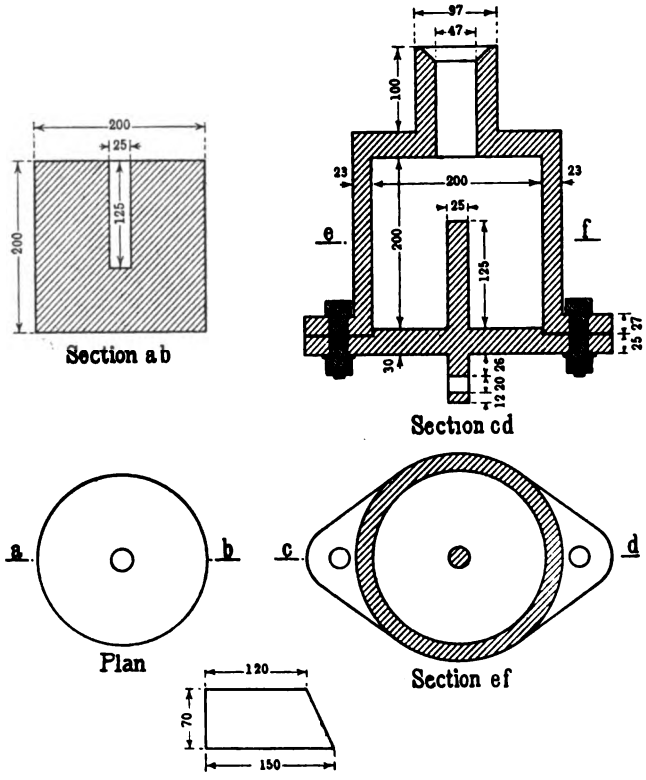

FIG. 88. Trauzl Lead Block Test

"*Interpretation of the Results.* (1) Lead block tests can only claim to give satisfactory comparative results when they are made with the same class of high explosive. If there be great differences in the speed with which the pressure develops, the results are no longer comparable.

"(2) Statements as to the strength of explosives should always be based on at least three determinations.

"(3) The reliability of the test is affected considerably: (*a*) By the

[1] The enlargement caused by a detonator alone under the same conditions is also deducted sometimes.—A. M.

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uniformity of the temperature of the lead at the time of the test. The standard temperature is 15° to 20° C.; (*b*) by the uniformity of the tamping; (*c*) by the uniformity of the test."

The lead block test has the advantage that it imitates fairly closely the conditions in a bore-hole, only unfortunately the charge has to be very small. The warning against using the test for the comparison of explosives with different velocities of detonation appears to be unnecessarily emphatic, for

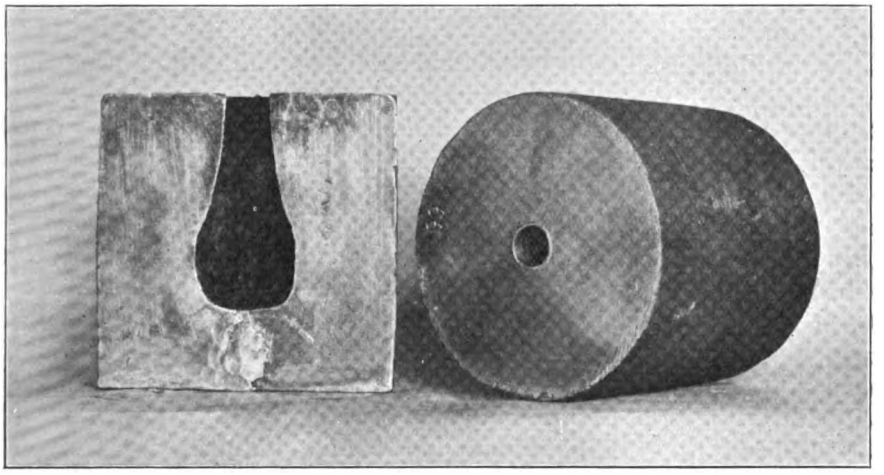

FIG. 89. Trauzl Lead Block after Test, and Section showing Expansion of Cavity by Explosive (from *Bureau of Mines Bulletin*, No. 15)

both Kast [1] and Dautriche [2] have found that the results are unaffected by variations in the density to which explosives are compressed, although this has a very great influence on the velocity of detonation. In the case of non-detonating explosives, such as black powder, the test fails, however, as the tamping is blown out before the full pressure is developed, or the gases escape through it, unless a more resistant tamping material be used, such as Portland cement. Probably the results are affected more by the temperature of explosion, the lead on the interior surface being eroded by the hot gases. For this reason aluminium explosives, which produce very high temperatures, give unduly high results in the lead block. If the lead blocks were weighed before and after the test, and the results corrected for the quantity of metal eroded away, it is possible that the figures would be more satisfactory.

Neumann gives the following as typical results with the Trauzl test: [3]

[1] *Spreng- und Zündstoffe*, p. 1030.
[2] *C.R.*, 144, 1907, p. 1032; *S.S.*, 1907, p. 313.
[3] *Ang.*, 1911, p. 2234.

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Nitro-glycerine	540 c.c.
Blasting gelatine	530 c.c.
Gelignite	420 c.c. (65 N/G, 25 $NaNO_3$, 8 W.M.)
Gesteins-Westfalit	380 c.c. (Ammonium nitrate exp.)
Picric acid	315 c.c.
Trinitro-toluene	290 c.c.
Safety gelatine dynamites	200–300 c.c.

Some of the modern safety explosives have been so far diluted to meet the requirement of the gallery tests, however, that they enlarge the cavity less than 200 c.c.

Kling and Florentin have found that the results are not affected appreciably by reducing the temperature of the explosive to −80° or even to −190°.[1]

Ballistic pendulum.

Another appliance, that is used to determine the comparative strength of explosives, is the ballistic pendulum. The Inspector of Explosives adopted it in England in 1900 in place of the Trauzl lead block for testing the strength of explosives for use in coal-mines. It is used for the same purpose by the U.S. Bureau of Mines, although they also carry out tests with the lead block. The latter is generally used on the Continent. The principle of the test consists in firing a stemmed shot from a steel gun into a heavy mortar, which is suspended from a bearing. The swing imparted to this pendulum is a measure of the power of the explosive. The pendulum at the Rotherham Testing Station consists of a 13-inch mortar weighing 5 tons 1 cwt., suspended at a distance of 92 inches from a roller bearing. A charge of 4 oz. of the explosive is loaded into a gun, such as was used in the Woolwich test for permitted explosives, and tamped in a standard manner. The gun is wheeled up until a distance of exactly 2 inches separates it from the mortar and is fired electrically with a detonator of the strength recommended by the makers of the explosive. The swing is measured, and is compared with that given by 4 oz. of 60 per cent. gelignite under the same conditions. This standard produces a swing of 3·27 inches.

The American Bureau of Mines use a 12·2 inch mortar weighing 14 tons 2 cwt., suspended at a distance of $89\frac{3}{4}$ inches from a knife-edge bearing (*see* Fig. 90). The standard charge is 8 oz. of 40 per cent. American straight dynamite, which is stemmed with 1 lb. of dry clay. The gun is brought up to a distance of $\frac{1}{16}$ inch from the mortar and fired electrically. The standard explosive produces a deflection varying between 2·7 and 3·1 inches, the result being affected by the wind, the exact position of the knife-edges, and other causes. Some charges of the standard explosive are fired on every day that tests are carried out to establish the "unit swing" for the day. Charges of the explosive under test are then fired until it is ascertained what will give about the same swing. Three of these charges are then fired, and from the

[1] *P. et S.*, vol. xvii., 1913, p. 151.

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mean the charge that would produce exactly the unit swing is calculated by simple proportion.

The momentum acquired by the pendulum is equal to $2\,W \sin\frac{a}{2} \times \sqrt{\frac{r}{g}}$, where W is the weight of the pendulum, a the angle through which it is

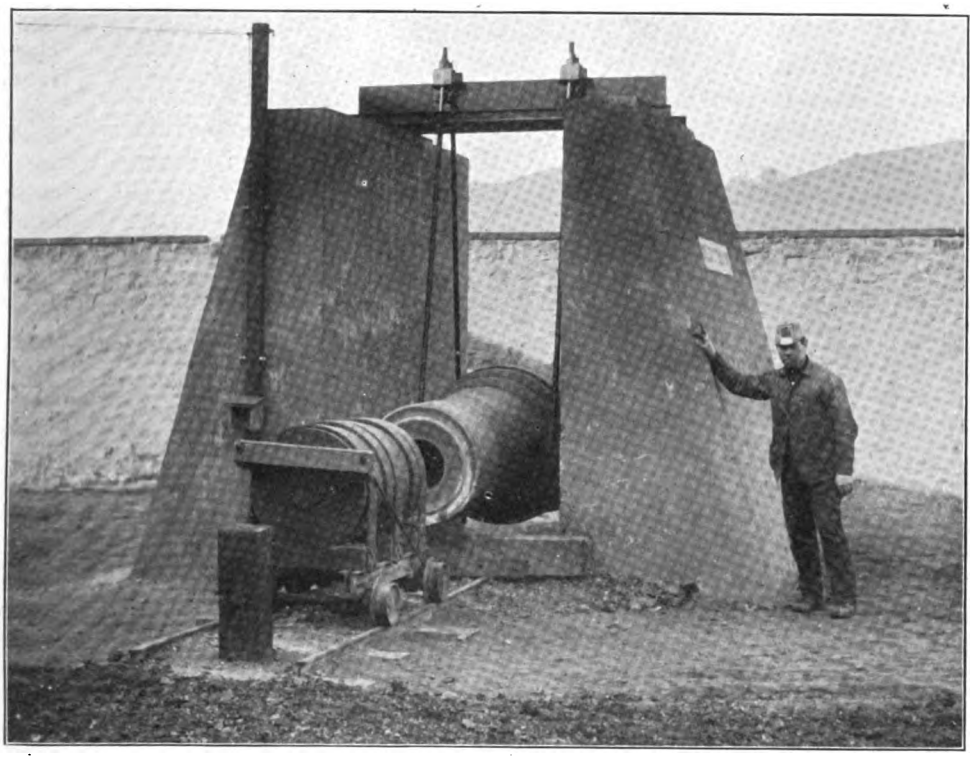

FIG. 90. Ballistic Pendulum (from *Bureau of Mines Bulletin*, No. 15)

deflected from the vertical, r its radius, and g the acceleration due to gravity. For small deflections we may write $2 \sin\frac{a}{2} = \frac{s}{r}$, where s is the linear deflection of the centre of gravity of the pendulum from the vertical. Hence the momentum is $\frac{W s}{\sqrt{g r}}$, and as W, r and g are all constant the momentum is proportional to s. If the stemming and all the products of explosion were brought to rest within the mortar, their momentum would be equal to that imparted to the mortar. But the gaseous products and part of the solids are blown out again and so must impart more momentum.

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One of the advantages that led to the adoption of the ballistic pendulum in place of the lead block at the Home Office Testing Station is that it gives a truer measure of the relative strengths of detonating and non-detonating explosives. The swing given by 4 oz. of dynamite was found to be 2·3 times as great as that given by the same quantity of black powder, whereas the average of the estimates given by seventy-two practical miners was 2·29.[1] The ratio given by Bichel's measurements of the pressure (*see* above) is 48·2/18·7 = 2·58.

In 1906 a large number of practical comparative trials were carried out in coal-mines with four different safety explosives in connexion with the Bobbinite inquiry, and it was found that the quantities of coal got were in very close agreement with the results that had been obtained with the ballistic pendulum :[2]

Explosive	Coal-getting trials	Ballistic pendulum
Bobbinite . . .	100	100
Carbonite . . .	177	159
Saxonite . . .	257	246
Ammonite . . .	273	261

There is a modification of this test in use, in which the explosive is fired from a suspended mortar, which has a bore that is several inches in diameter near the muzzle, but is contracted further in. The charge is placed in the narrow portion, and over it is placed a round or cylindrical shot, which fills the wide part of the bore. On firing, the mortar recoils a distance, which is taken as a measure of the power. Comey and Holmes have found that the results are much more uniform, if before each test two shots are fired with blasting gelatine so as to clean out the bore of the mortar very thoroughly.[3]

THE TIME FACTOR

These methods of determining the power of explosives all leave out of account one very important factor, the time required for the explosive to develop its maximum pressure. For some purposes this is of the very greatest consequence : in the case of detonators, for instance, the violence of the blow is of more importance than the total quantity of energy liberated : and for hasty military demolitions, where it is not possible to tamp the charge properly, a very rapidly detonating explosive is also required. On the other hand, for blasting comparatively soft material such as coal, which must not be broken up too much, the explosive should not be too violent.

It has been proposed by Bichel[4] to use the expression $\frac{m v^2}{2}$ for the "brisance"

[1] See *A.R.*, 1900, p. 129.
[2] *A.R.*, 1906, p. 108.
[3] *8th Int. Cong. Appl. Chem.*, 1912, vol. xxv., p. 209.
[4] *S.S.*, 1908, p. 343.

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or violence of the blow given by an explosion, m being the mass of gas evolved and v the velocity of detonation. But practical tests do not confirm the idea that the effect is proportional to the square of the velocity of detonation: simple proportionality agrees with the facts better. Moreover, the above expression represents a quantity of energy, that is to say, it has the same dimensions as the indications of the pressure gauge, the lead block and the ballistic pendulum, but what we are now seeking is the intensity of action of an explosive when detonated unconfined. Experiments upon the crushing of small lead cylinders indicate that this can be represented approximately by an expression K.PV.U.D, where P is the pressure developed by the explosive, when detonated in a comparatively large volume V, U is the velocity of detonation, D is the density of the explosive, and K is a constant.[1] The matter is, however, complicated by the fact that the brisance of a cartridge is different in different directions: if a cylindrical cartridge be detonated from one end, the action in the direction in which the detonation proceeds is considerably greater than in the opposite direction. Thus Kast found that a charge of trinitro-toluene detonated in an upright position over a lead cylinder reduced its length 2·81 mm. when the detonator was at the top, and only 1·73 mm. when it was at the bottom of the cartridge. Taffanel and Dautriche have also shown the great difference in the shock produced from the two ends of a cartridge,[2] as revealed by the far greater distance at which a second cartridge can be detonated by influence, according to relative position:

Explosive	Direct detonation Second cartridge		Inverse detonation Second cartridge	
	Exploded at cm.	Did not explode at cm.	Exploded at cm.	Did not explode at cm.
Grisoutine . . .	30	40	10	20
Grisoulite-roche . .	5	8	—	1
Grisoulite-couche salpétrée .	5	8	1	2
Carbite d'Ablon . .	12	16	1	2

Soon after the invention of the first high explosives the importance of measuring the rate of detonation was appreciated, and experiments of this sort were carried out by Abel, Berthelot, and others. The method adopted consisted in detonating a long string of cartridges, near the two ends of which wires were passed through the explosive. These were connected to the two circuits of a Boulengé or other chronograph, and so a record was obtained of the time that was required for the detonation to travel between the two

[1] *See also* Kast, *S.S.*, 1913, p. 65.

[2] *C.R.*, 153, 1911, p. 823.

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points selected. But as these chronographs only give readings to a few 10,000ths of a second, and in this time the detonation travels a metre or more, it was necessary to make the train 35 or more metres long to obtain an accurate result.

Mettegang recorder.

A better method was devised by Mettegang, who adapted the idea of Noble's chronoscope.[1] The record is obtained by means of induction sparks on a smoked drum, which is rotated rapidly by means of an electric motor. The drum is provided with a speed recorder and a device for measuring small distances on it. The latter consists of a microscope with spider line for observing the surface of the drum, which is moved round by an endless screw fitted with a dial. Each complete rotation of the screw corresponds to 1 mm. on the surface of the drum. It is rotated until one of the spots made by an induction spark comes under the spider line of the microscope. On the dial the position can then be read to 0·01 mm. The position of the spot made by one of the other induction circuits can then be ascertained in the same way. As the drum can be rotated by the electric motor with a peripheral velocity of 100 metres per second, readings can be obtained to one 10,000,000th part of a second. It is possible with this to measure the velocity accurately with a string of cartridges 1 metre long, or even half this, and obtain an approximate estimate with considerably shorter trains. The apparatus is arranged for six different induction circuits. The primary circuits pass through wires crossing the train of explosive at different points, and are supplied with current from an accumulator. When this current is interrupted by the breaking of the wire, a current is induced in the corresponding secondary circuit, one wire of which is in permanent contact with the drum, and the other terminates in a platinum point, which is brought quite near to its surface.[2]

The sources of error of an apparatus of this type have been examined by Kast.[3] The wire passing through the explosive should be as thin as possible; Kast used copper wires 0·1 mm. thick. They should be fastened as firmly as possible. When the explosive was detonated in metal tubes Kast passed the wires through little vulcanite plugs in the walls, pulled them tight and wound them on to the outside of the plugs before joining them to the connecting wires. Similarly when the explosive was detonated without envelope, it was laid in a wooden trough and the thin wires were fastened firmly to nails, and made to pass either through the explosive, when it was soft, or over its surface in the case of such substances as cast picric acid. The distance of the platinum points from the surface of the drum should only be about 0·1 mm., to avoid danger of the spark springing to one side. The different circuits should, of

[1] *Trans. Roy. Inst.*, 1871.

[2] For further descriptions *see* Mettegang, *Report of 5th Cong. Appl. Chem.*, vol. ii., p. 327; *Glückauf*, 1904, p. 1046; Kast, *Spreng- und Zündstoffe*, p. 1025; Bichel, *Testing Explosives*, Chapter V; *S.S.*, 1908, p. 403; Hall, *Bureau of Mines Bulletin* 15, p. 92.

[3] *S.S.*, 1913, p. 91.

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course, be as similar as possible one to another. The currents should be equal and steady, and should proceed in the same direction in all cases. The mark on the drum is never made at the same instant as the detonation wave reaches the wire : there is always a delay due to various causes, which although

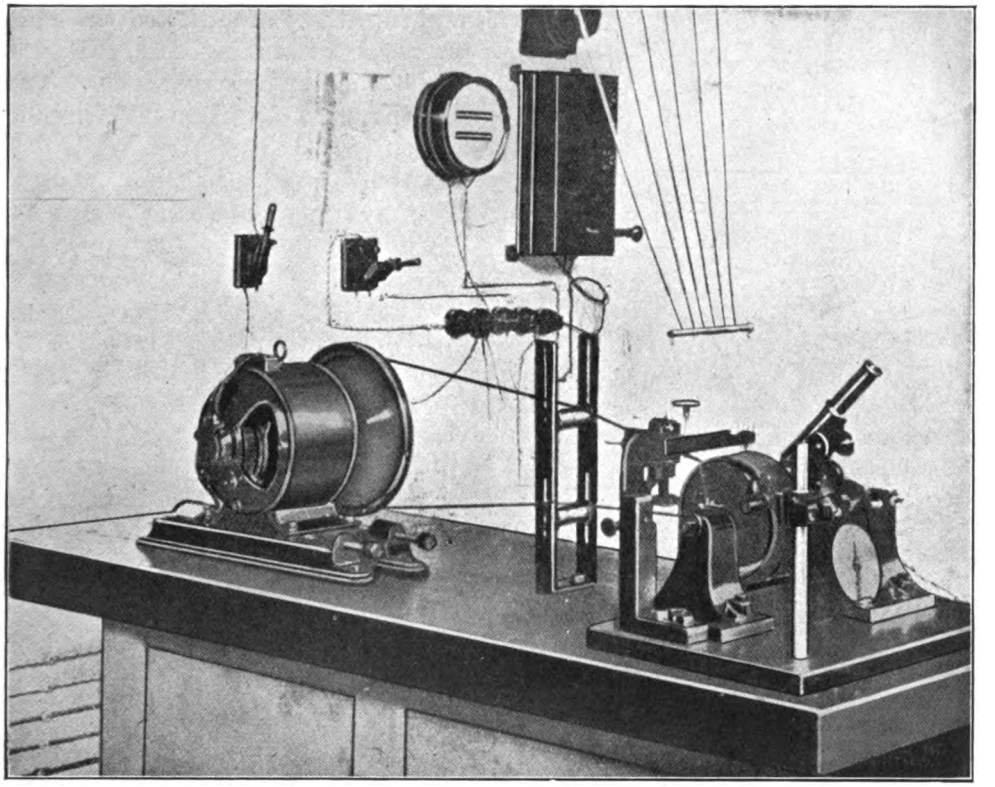

FIG. 91. Mettegang Time Recorder for Determining the Velocity of Detonation

short in actual duration, is long compared with the sensitiveness of the instrument. Hence the great necessity to have the causes of delay equal in all the circuits. In order to diminish the self-induction in the circuits, which is one of the causes of delay, the iron cores of the induction coils have been done away with at the American Testing Station.

Dautriche's method.

A very simple and ingenious method of measuring the velocity of detonation has been devised by Dautriche.[1] It is based upon the use of detonating fuse, the rate of detonation of which is very uniform and is determined by the manufacturers, MM. Davey, Bickford, Smith et Cie, by the method described

[1] *C.R.*, 143, 1906, p. 641.

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above. The arrangement of the test is shown in Fig. 92. The explosive is compressed into the tube z to a known density, and into one end a detonator d is inserted. Two other detonators are inserted into the sides of the tube at a distance from one another of 100 mm., or other selected interval, and into these are inserted the ends of two pieces of detonating fuse, AF and BG 1000 and 800 mm. long respectively. The other ends of these pieces of fuse lie alongside one another on a slab of lead P for a distance of about 200 mm. The mid-point E between F and G is marked on the surface of the lead. When the explosive is detonated by means of the first detonator, the detonation is communicated to the two pieces of fuse, and the point where the two waves of detonation meet is shown by a sharp line S, which is formed on the surface of the lead. The distance ES is measured, and the velocity of detonation can then be calculated from the formula

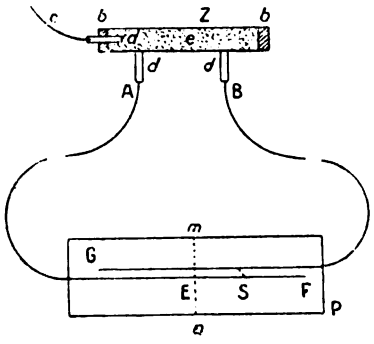

FIG. 92. Dautriche's Method for determining the Velocity of Detonation

$$V = U \times \frac{AB}{200 + 2 \times ES}$$

where U is the known velocity of detonation of the fuse, and V is the velocity of detonation of the explosive under examination. More often now only one piece of fuse is used, both ends of which are inserted into detonators at different points in the cartridge of explosive. The middle part of the fuse is firmly attached to the slab of lead, and the centre point M of the fuse is marked. We then have

$$V = U \times \frac{AB}{2 \times MS}$$

By this method the velocity of detonation can be determined on a single cartridge of the explosive. This is a doubtful advantage, when it is desired to ascertain the intrinsic velocity of the material, as there are great fluctuations in the first part of the charge, but it is of great advantage in ascertaining the actual time that a mining charge takes to detonate.

Velocity of sound.

The velocity of the wave of detonation is of the same order as the velocity of sound waves through solids : in iron this is about 5130 metres per second, and in wood up to about 5000. This velocity may be calculated from the equation

$$v = \sqrt{\frac{\mu}{d}}$$

where μ is Young's modulus of elasticity and d is the density. At very high

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pressures the value of μ is increased, especially in the case of gases and liquids. The above equation shows that the direct effect of increase of density would be

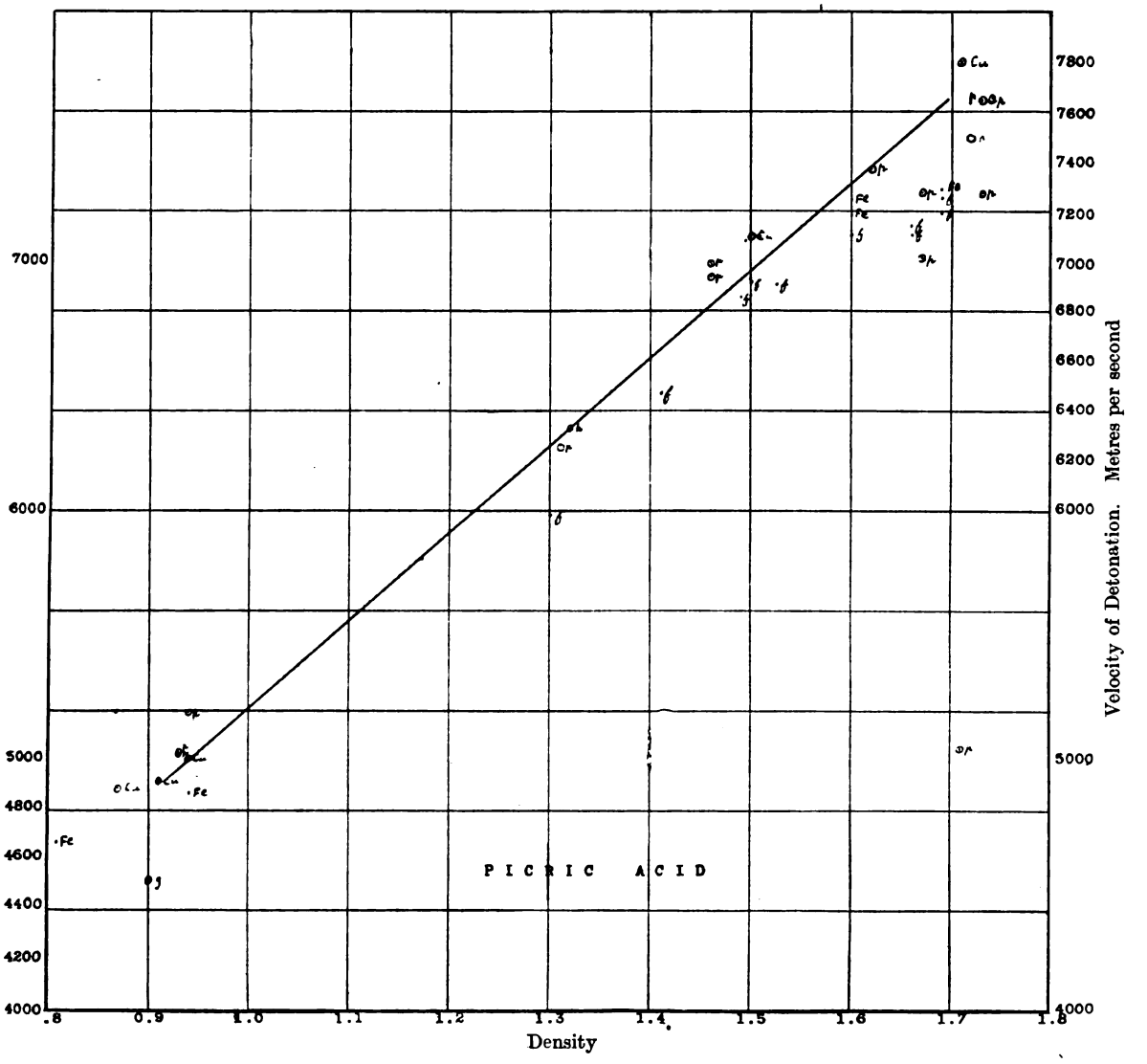

FIG. 93. Velocities of Detonation of Picric Acid

to decrease the velocity, but it also acts indirectly in two ways: it no doubt increases the modulus of elasticity, and there is also an increase in the pressure

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developed, and this further raises the value of μ. The increase in the modulus of elasticity is a cause of the diminution in sensitiveness, for the impulse given by the detonator is more rapidly dispersed, before the explosive has time to start detonating. Moreover, when there are numerous small air-spaces in the explosive, the waves of compression are reflected back from the boundaries of each of them, and the effect of the detonator is consequently more concentrated.

Influence of density.

The velocity of detonation of an explosive is not a constant quantity, but is affected by various conditions, the most important of which is the density of the explosive. The variation of the velocity of detonation with density in the case of cheddite containing ammonium perchlorate was shown in Fig. 70. Very similar curves have been obtained with other Cheddites, but the fall in the velocity, when the critical density is passed, is apparently due entirely to the insensitiveness of the dense explosive, which renders it impossible to detonate it completely. If complete detonation could be obtained, the velocity would probably continue to rise up to the highest attainable density. Figs. 93, 94, 95 show the effect of variations of density on the velocity of detonation of picric acid, trinitro-toluene and trinitro-benzene based on the determinations of Dautriche [1] and Kast.[2] Both authors have drawn curves to represent their results, but an examination of the data leads only to the conclusion that it is approximately a straight line even up to the greatest densities that can be attained.

Influence of diameter.

Other causes which increase the pressure also produce an increase in the velocity of detonation up to a limit. Thus, if the diameter of the column of explosive is too small, there is a diminution in the velocity, but with unmixed nitro-derivatives a diameter of 10 mm. is sufficient to obtain the maximum value. Thus, Kast obtained the following results with cast trinitro-toluene of specific gravity 1·59 in iron tubes fired with a 1 g. detonator and a priming of compressed picric acid (density 1·58):

Diameter of explosive mm.	Velocity of detonation M/sec.
21	6700, 6555
29	6700
75	6595 mean of 3 experiments
160	6690
220	6675
300	6710
Mean	6649

[1] *P. et S.*, vol. xvi. p. 27, observations marked ⊙.
[2] *S.S.* 1913, pp. 65, 88, 133, 155 and 172. marked •.

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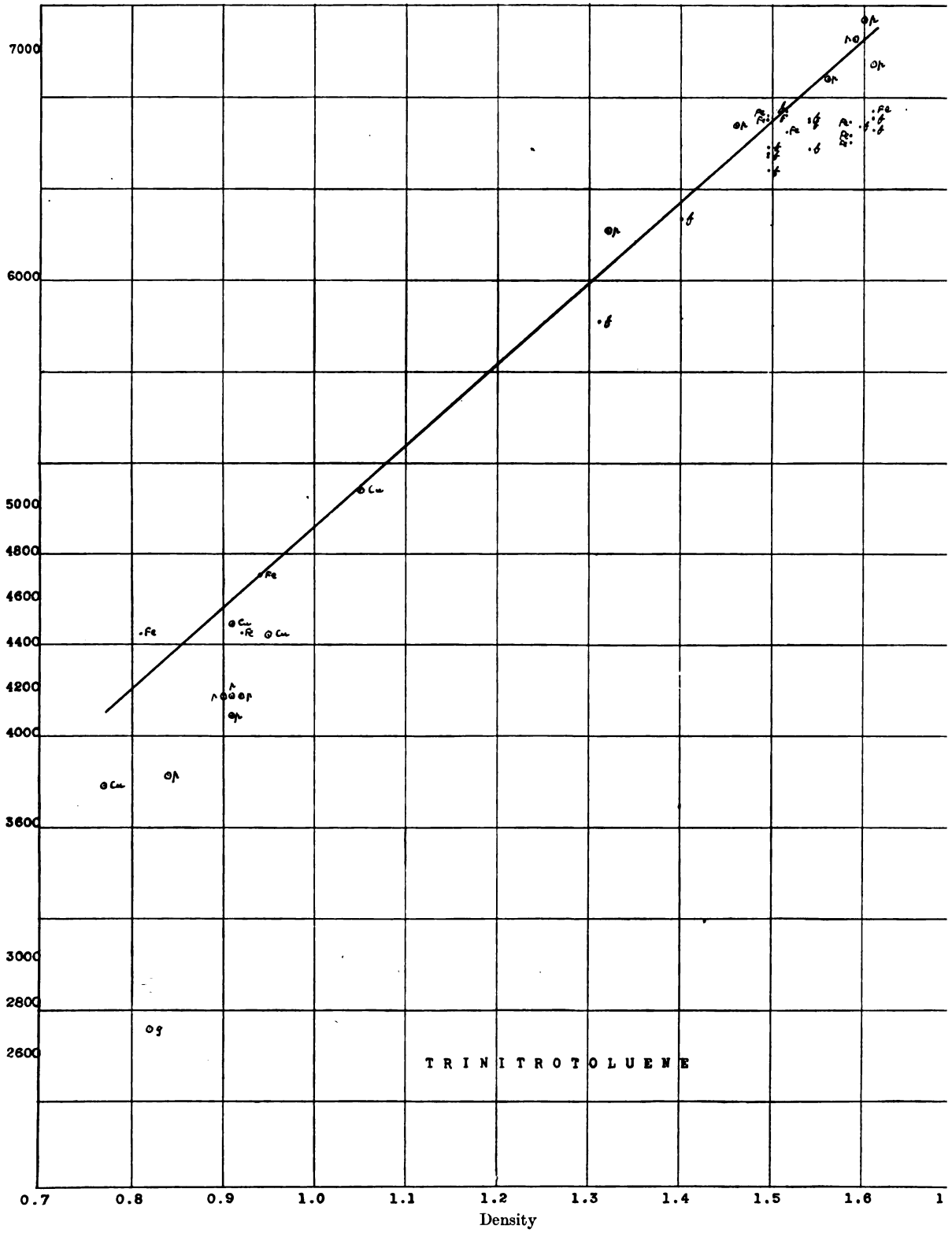

FIG. 94. Velocities of Detonation of Trinitro-toluene

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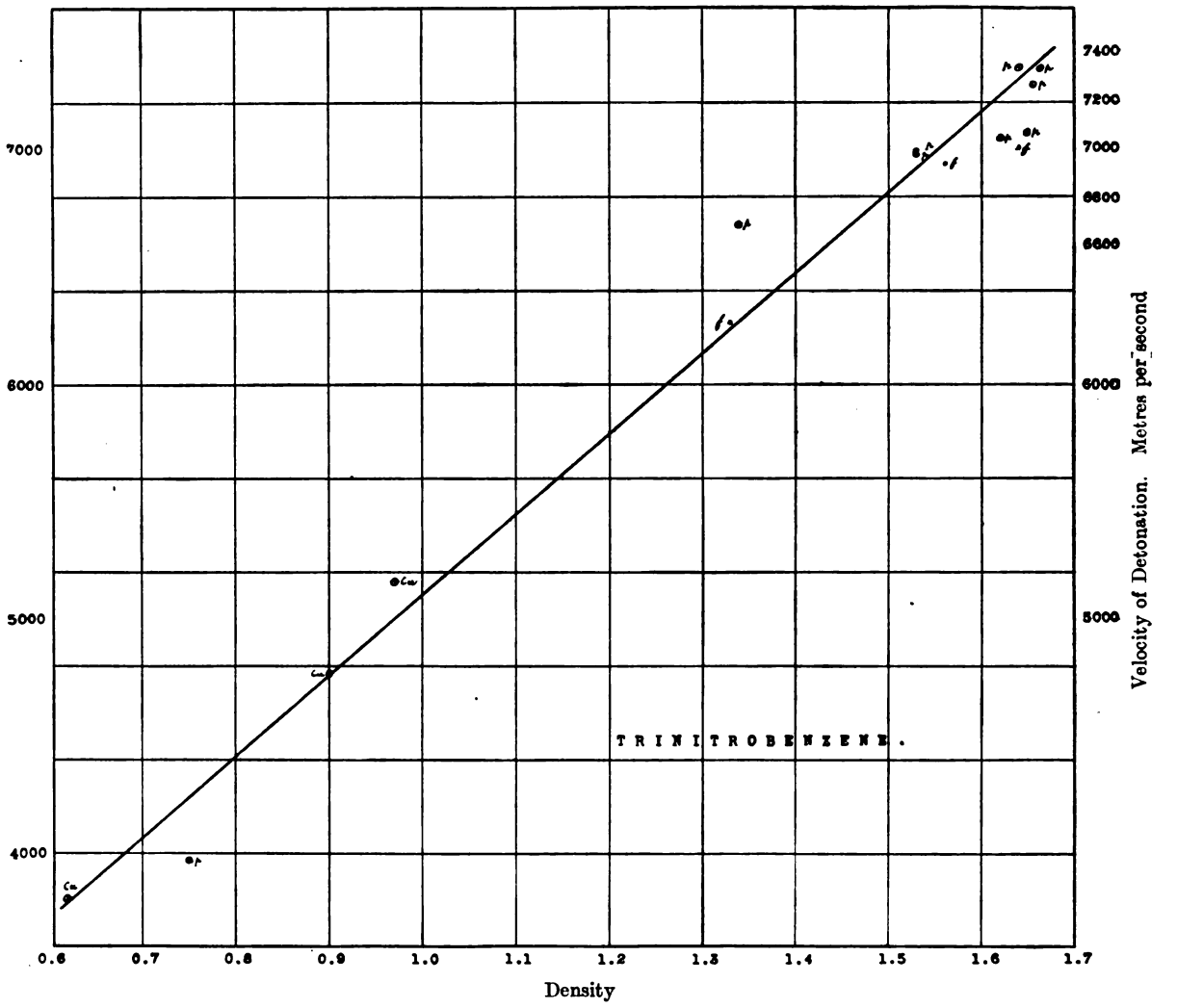

FIG. 95. Velocities of Detonation of Trinitro-benzene

But with the more insensitive explosives the influence extends to somewhat larger diameters. With ammonium nitrate explosives fired by means of 2 g. detonators in iron tubes the following results were obtained :

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Explosive			Density	Velocity of detonation in tubes of diameter		
				26 mm.	40 mm.	50 mm.
Aldorfit	Ammon. nitrate	81	1·10	—	4825	—
	Trinitro-toluene	17	1·14	4410	—	—
	Rye meal	2	1·15	4430	—	—
			1·16	—	4925	—
			1·17	—	—	4960
Gesteinsdorfit	Ammon. nitrate	66	1·10	3940	—	—
	Potas. nitrate	5	1·11	—	4420	—
	Trinitro-toluene	15	1·15	4045	4505	—
	Sod. chloride	10	1·17	—	—	4605
	Rye meal	4	—	—	—	—

Influence of envelope.

On Figs. 93, 94, 95 are marked the nature of the envelopes surrounding the columns of picric acid, trinitro-toluene and trinitro-benzene, when they were detonated. *Fe* means iron tube, *Cu* copper tube, *p* paper, *g* glass, and *f* free. It will be seen that with these explosives the velocity of detonation was not much affected by the strength of confinement. With ammonium nitrate explosives the effect is much greater, thus Bichel has recorded the following results :

Explosive	Velocity of detonation	
	Unconfined	Confined
Donarite	3930	4137
Ammon-carbonite I.	1753	3195
Ammon-carbonite	1649	3094
Thunderite	2137	3654

Influence of primer.

The strength of the detonator or priming has but little ultimate influence, provided that it be strong enough to start the wave of detonation, but at the commencement of the train there are often great irregularities : the velocities there may be either high or low, according to the strength of the igniter. Thus with cast trinitro-toluene, specific gravity 1·60, in iron tubes Kast obtained the following results in different parts of the columns :

Priming	Velocity of detonation measured over the distance			
	100–200 mm.	200–405 mm.	405–505 mm.	
65 g. picric acid (1·58)	3910	6415	5710	
950 g. trinitro-toluene (1·54)	10580	6880	5080	
	10–160 mm.	160–310 mm.	310–460 mm.	460–1060 mm.
21 g. picric acid (1·58)	5420	5795	6330	6590
600 g. trinitro-toluene (1·45)	7520	6000	6680	6590

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The velocities measured over very short distances are not very accurate, but the above figures are in all cases the means of three different experiments yielding similar results. With moderate ignition the results are fairly uniform, as is shown by the following velocities recorded on the section 340 mm. to about 1060 mm. with trinitro-toluene (specific gravity 1·53 to 1·54) :

0·65	g.	detonator	missfires
0·8	g.	,, ...	6570
1·0	g.	,, ...	6650
1·5	g.	,, ...	6540
2	g.	,, ...	6570
3	g.	,, ...	6560
1	g.	detonator and 10 g. picric acid (1·58)	6800

When the velocity has attained its proper value, it remains constant over an indefinite length :

Section	Picric acid 1·60 1 g. detonator	Trinitro-toluene 1·52 1 g. detonator and 10 g. picric acid
20–1020 mm. . . .	7100	6740
1020–2020 mm. . . .	7154	
2020–3020 mm. . . .	7054	6630
3020–4020 mm. . . .	7100	6710
4020–5020 mm. . . .	7010	6755

The more insensitive explosives are, however, incapable of maintaining the velocity of detonation. Thus Monachit, consisting of 81 per cent. ammonium nitrate, 13 per cent. liquid nitro-derivatives, 5 per cent. saltpetre and 1 per cent. flour, gave :

Density	Velocity of detonation in section			Ignition
	150–250 mm.	250–630 mm.	630–730 mm.	
1·02 . .	4885	4440	3345	2 g. detonator
1·35 . .	4230	3495	3135	2 g. detonator and 140 g. T.nt.
1·56 . .	4745	1730	1270	2 g. detonator and 127 g. T.nt.

Even explosives such as picric acid show signs of behaving in the same way at the highest densities, whether they be cast or compressed.

The temperature of the explosive has little or no influence on the velocity

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of detonation, although it affects the sensitiveness considerably (*see* p. 359). The following results were obtained by A. Kling and D. Florentin [1]: **Effect of temperature.**

	Density	Velocity of Detonation	
		Ordinary temperature	About −190°
Fulminate	1·25	2250	2350
Cheddite No. 2	1·00	2365	2080
Picric acid	1·01	4470	4750

The velocities were determined by Dautriche's method; to ensure detonation the explosive in the neighbourhood of the detonator was not cooled.

Nitro-glycerine. The behaviour of liquid trinitro-glycerine is curious. The earlier determinations of its velocity of detonation gave very discordant results, and the matter was reinvestigated by Comey.[2] In a tube 6 mm. in diameter detonation from a 1·6 gr. detonator was only propagated a few inches. With a 9 mm. glass tube an average velocity of 654 metres per second was obtained, three tests being made with only comparatively small variations from the average. With 25 mm. iron tubes five tests were made, which fell into two groups, the results being 1539 and 1463, mean 1501 metres per second, and 6783, 7877 and 8410, mean 7690. In a 38 mm. iron pipe with a 1·6 gr. detonator the velocity was 8527 metres per second, but with a 0·8 gr. detonator the results were 1288, 2412 and 1627. Using a detonating fuse as primer, four closely concordant results were obtained averaging 7234 metres per second. Thus, two widely differing velocities were recorded with no intermediate values. Apparently under a moderate blow the elasticity of nitro-glycerine is that of a liquid, but under a very violent impulse it behaves like a solid. The velocity of sound in water is about 1440 metres per second at 13° and 1530 at 30°. Blochmann [3] gives the value 1525 metres per second for both di- and tri-nitro-glycerine.

Nitro-glycerine explosives. Comey also determined the velocities of detonation of a large number of American dynamites of various grades, and the results are given in Fig. 96. For the composition of these explosives *see* Chapter XXII. In the case of the "straight dynamites" the velocity increases steadily with the percentage of nitro-glycerine, and is not affected by variations in the strength of the detonators, nor by the use of primers. The gelatine dynamites differ from these in that the nitro-glycerine is gelatinized with a small proportion of nitro-cotton. When fired with detonators of various strengths, they detonate with a fairly uniform velocity of about 2270 metres per second irrespective of the percentage of nitro-glycerine. But if a primer of 40 per cent. straight dynamite be employed, the velocity is greatly increased, and a curve is obtained almost parallel to that of the straight dynamites, but higher. In the ammonia

[1] *P. et S.*, vol. xvii., 1913, p. 154.
[2] *Seventh Inter. Cong.*, 1909, IIIb, p. 30.
[3] *Bergbau*, 1905; *S.S.*, 1906, p. 80.

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dynamites a large part of the nitro-glycerine has been replaced with ammonium nitrate ; the velocity rises to a maximum with the 50 per cent. brand and then falls again. These results were not materially affected by the use of a primer.

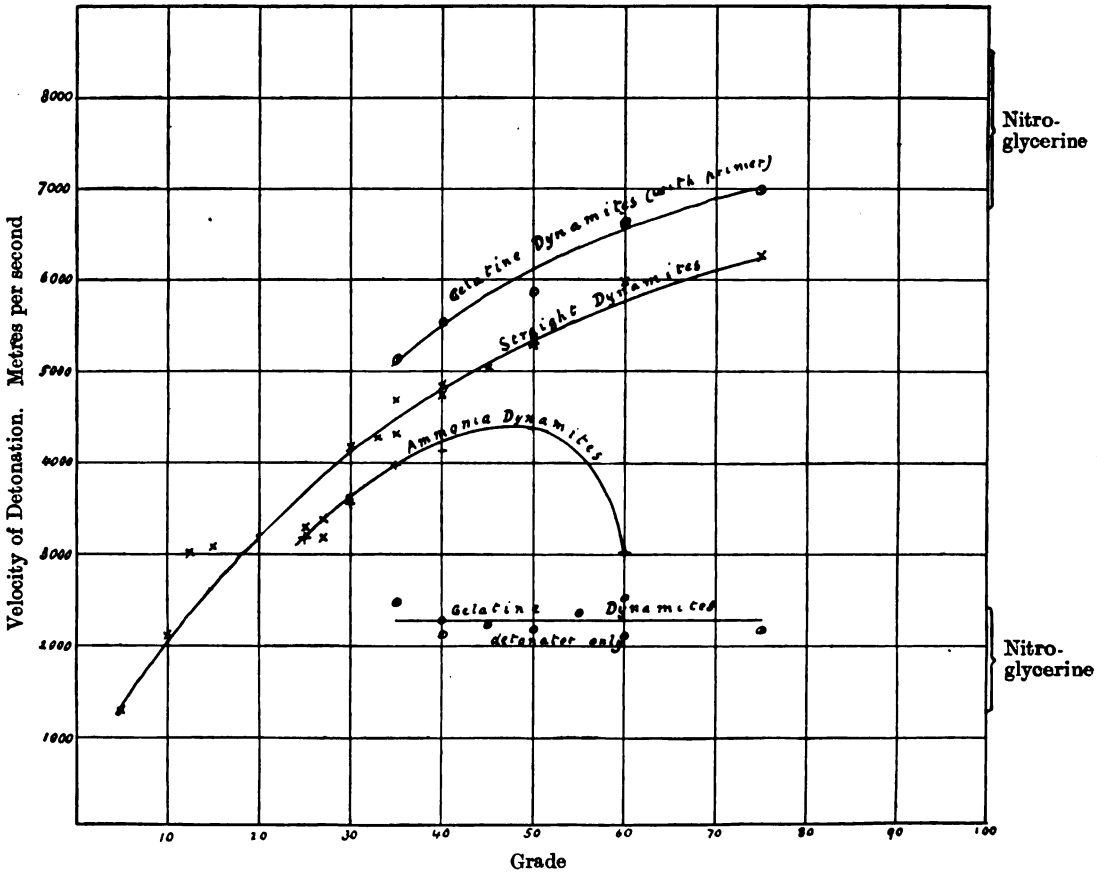

FIG. 96. Velocities of Detonation of American Dynamites

It is seen, therefore, that the gelatine dynamites, which are similar to the gelignites made in Europe, resemble nitro-glycerine itself in having two very different rates of detonation. Comey does not state the densities of the explosives.

The following Table gives the velocity of detonation of some other explosives :

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Explosive	Diameter mm.	Density	Velocity of detonation m./sec.	Authority
Mercury fulminate	6·45	—	3920	Bichel
Austrian detonating fuse (old pattern) containing mercury fulminate, water and glycerine	—	—	3000–3500	—
	—	—	4000–5000	Gen. Hess
Austrian detonating fuse M 03 — Hg. fulminate 80, Paraffine 20	—	—	5000–6000	Gen. Hess
	—	—	—	—
French detonating fuse (old pattern) — Picric acid powdered in tin tube	—	—	7000	—
(new pattern) — T/n/t cast in lead tube	—	—	6000–6500	—
	4·3–4·5	1 5	4800–4990	Bichel
Italian detonating fuse — Ballistite and Black powder	5·5	—	5000	—
Gun-cotton	2	·69–·73	3700–3800	Berthelot
	< 4	·9	3900	,,
	2	1·17	4800	,,
	< 4	1·2	4300	,,
	3·1	1·27	5400	,,
	< 4	1·4	4800–6200	,,
	—	1·25	6380	Bichel
	23	·82	5220	Abel
Gun-cotton, wet — 15 per cent. water	23	—	5540	Abel
30 per cent. water	23	—	5830	,,
,, ,,	31	—	5230	Bichel
Nitro-hydro-cellulose	4	—	4900	
	5·5	—	6100	
Nitro-starch	4	1·1–1·2	5000	Abel
	4	1·35	5500	Berthelot
Nitro-mannite	4	1·5	6900–7100	
	4	1·9	7700	
Tetranitro-methylaniline	—	—	8455	Bichel
	21	1·53	7075–7215	Kast
	21	1·57	7155	,,
	21	1·63	7215	,,
Trinitro-chlorbenzene (compressed)	21	1·70–1·71	6855	,,
	21	1·72–1·73	6960	,,
	21	1·74–1·75	7130	,,
,, ,, (cast)	29	1·76	7150	,,
Hexanitro-diphenylamine	21	1·58	7100	,,
	21	1·67	7150	,,
Trinitro-cresol	21	1·52	6620	,,
	21	1·54	6400	,,
	21	1·62	6850	,,

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Explosive			Diameter mm.	Density	Velocity of detonation m./sec.	Authority
Dinitro-benzene (confined)			21	1·4	6160 (?)	,,
			21	1·5	6000	,,
Methyl nitrate			3	1·18	2100	Berthelot
Panclastite . . . $CS_2 + N_2O_4$ . .			3	1·35	4600–6600	,,
NITRO-GLYCERINE EXPLOSIVES						
Dynamite No. 1	N/G	75	3	—	2300–2800	Berthelot
	Guhr	25	6	—	1900–3200	,,
			30	1·58	6820	Bichel
			20	·63	1990	Dautriche
			20	·79	2400	,,
			20	·85	2560	,,
			20	1·34	3670	,,
			20	1·54	5230	,,
			20	1·62	6800	,,
			20	1·69	4200	,,
			20	1·71	2460	,,
			20	1·74	failed	,,
			—	1·39	6370	Kast
			26	1·43	2680–6040	,,
Blasting gelatine	N/G	92–3	30	1·63	7700	Bichel
	Col. Cot.	7–8	—	1·58	1535	Kast
			—	—	1800–4000	Mann
Gelatine dynamite	N/G	62–63·5	30	1·67	7000	Bichel
	Col. cot.	1·5–3	—	1·59	2055	Kast
	$NaNO_3$	27	—	—	2000–2300	Mann
	Wood-meal	8				
Dynamite 50 per cent. No. 3	N/G	50	—	1·56	4610	Kast
	Guhr	7				
	KNO_3	33·1				
	Wood-meal	9·7				
	Chalk	0·2				
Dynamite 40 per cent.	N/G	40	—	1·56	4440	Kast
	$NaNO_3$	42				
	Wood-meal	16·7				
	Chalk	1·2				
Extra-Carbonite	N/G	35	—	1·13	3970	Kast
	Col. cot.	0·3	—	1·20	4070	,,
	$Ba(NO_3)_2$	4				
	KNO_3	25·5				
	Tan meal	34·8				
	Soda	0·5				
Carbonite II.	N/G	30	—	1·05	3720	Kast
	$NaNO_3$	24·5	—	1·10	3850	,,

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Explosive			Diameter mm.	Density	Velocity of detonation m./sec.	Authority
Carbonite II. (*cont.*)	Flour	40·5	30	1·49	2470	Bichel
	$K_2Cr_2O_7$	5				
Nobel's	N/G	30	—	1·16	3860–3930	Kast
Wetter-dynamite I.	$NaNO_3$	31				
	Flour	30				
	Wood-meal	6				
	Naphthalene	2				
	Alum	1				
Nobel's	N/G	25	—	1·18	3350	Kast
Wetter-dynamite II.	$NaNO_3$	32	—	1·25	3750	,,
	Flour	34				
	Wood-meal	3				
	Veg. oil	1				
	Alum	5				
Kohlen-Carbonite	N/G	25	—	1·16	3160	Kast
	KNO_3	34	30	1·42	2700	Bichel
	$Ba(NO_3)_2$	1				
	Flour	38·5				
	Tan meal	1				
	Soda	0·5				
Carbonite I.	N/G	25	30	1·55	3042	Bichel
	$NaNO_3$	30·5				
	Flour	39·5				
	$K_2Cr_2O_7$	5				
Carbonite	N/G	25	30	1·08	2440	Bichel
	KNO_3	30·5				
	$Ba(NO_3)_2$	4				
	Wood-meal	40				
	Soda	0·5				
AMMONIUM NITRATE EXPLOSIVES CONTAINING NITRO-GLYCERINE						
Gelatine Carbonite	N/G	25·3	30	—	2300	Bichel
	Col. cot.	0·7				
	NH_4NO_3	41·5				
	Glyc. gel.	6·9				
	NaCl	25·6				
Donarite	N/G	3·8	26	0·89	3700[1]	Kast
	Col. cot.	0·2	26	0·9	3770[1]	,,
	NH_4NO_3	80	30	1·31	4140[1]	Bichel
	T/n/t	12	30	1·31	3930[2]	,,
	Flour	4				
Donarite with Am. oxalate	Donarite	85	26	1·01	4100–4240	Kast
	Am. ox.	15				

[1] In iron tube. [2] Unconfined.

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Explosive			Diameter mm.	Density	Velocity of detonation m./sec.	Authority
Ammon-carbonite	N/G	4	40	1·06	3380	Kast
	NH_4NO_3	82	26	1·23	3310	,,
	KNO_3	10	30	1·19	3100	Bichel
	Flour	4	30	1·19	1650[1]	,,
Ammon-carbonite I.	N/G	4	30	1·11	3195	Bichel
	Col. cot.	0·2	30	1·11	1753[1]	,,
	NH_4NO_3	80·3				
	KNO_3	5				
	Starch	4·5				
	Coal dust	6				
	AMMONIUM NITRATE EXPLOSIVES					
Thunderite	NH_4NO_3	92	30	1·07	3650	Bichel
	T/n/t	4	30	1·07	2137[1]	,,
	Flour	4				
Dynammon	NH_4NO_3	90	26	1·01	4100–4240	Kast
	Red Charcoal	10				
Westfalite	NH_4NO_3	91	26	0·90	3830	Kast
	KNO_3	4	40	1·01	4350	,,
	Resin	5	26	1·06	failed	,,
Dahmenite A.	NH_4NO_3	90·8	26	1·02	3680	Kast
	$K_2Cr_2O_7$	2·2				
	Naphthalene	6·5				
	Curcuma	0·5				
Permonite	NH_4NO_3	42·5	26	1·05	3690	Kast
	T/n/t	10	26	1·13	3780	,,
	$KClO_4$	32·5				
	Starch	12				
	Wood-meal	3				
Aluminium explosive	NH_4NO_3	44·9	21	1·68	4850	Kast
	T/n/t	31				
	Al wool	24·1				

[1] Unconfined.

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EFFECT OF ADDITIONS ON THE VELOCITY OF DETONATION OF AROMATIC NITRO-EXPLOSIVES (KAST)

Mixture			Conditions	Diameter	Density	Velocity of detonation	Velocity of detonation of principal constituent at same density
Tetranitro-methylaniline Dinitro-benzene		63 37	Compressed Unconfined	21	1·58	6960	7160
T/n/t D/n/t		90 10	Compressed or cast In iron tube	21–29	1·56–1·59	6620	6680
T/n/t D/n/t		50 50	In iron tube: Compressed In iron tube: Cast	21–29 21–29	1·52 1·52	6220 failed	6660 —
Plastrotyl	T/n/t Resin	99·5 0·5	Pressed into iron tube	26	1·33	5520	5920
Macarite	T/n/t $Pb(NO_3)_2$	30 70	Unconfined	21 21	2·73 2·89	4700 4850	— —
Triplastite	T/n/t D/n/t Col. cot. $Pb(NO_3)_2$	70 1·2 28·8	Pressed into iron tube	26	1·45	5030	6400

In Kast's experiments the nitro-glycerine and ammonium nitrate explosives were always fired with a 2 g. detonator, but the aromatic nitro-explosives were detonated by means of a primer of loosely compressed picric acid or trinitro-toluene. In the case of the nitro-glycerine explosives, the velocity of detonation is seen to be dependent largely on the percentage of nitro-glycerine. But the addition of nitro-glycerine to ammonium nitrate explosives does not seem to affect the velocity of detonation to any great extent. The addition of dinitro-derivatives to the more highly nitrated compounds does not affect the velocity much more than the simple reduction of density would. Lead nitrate, on the other hand, reduces the rate of detonation considerably.

Brisance meter.

There are other simpler tests for ascertaining the comparative brisance of explosives. The one that is most satisfactory is probably that in which the crushing effect on metal cylinders is measured. A test devised by Hess and used in Austria consists in detonating a charge of 100 g. on the top of two lead cylinders supported on a heavy iron base.[1] The shortening of the upper cylinder is taken as a measure of the brisance, whereas that of the lower one is supposed to be affected more by the pressure exerted. In the Prussian Military Research Department the conclusion was arrived at that the results were not always satisfactory, and a different form is used there,

[1] *See* Guttmann, *Manuf. of Expl.*, vol. ii., p. 357 ; Berger, *S.S.*, 1906, p. 151.

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which is shown in Fig. 99.[1] On the steel base *a* there is fitted a hollow steel cylinder *b*, in which moves a tightly fitting steel piston *c*. This carries a strong nickel steel plate *d* 20 mm. thick and weighing 320 g., which is protected above by two round lead discs 4 mm. thick, on which the explosive is detonated,

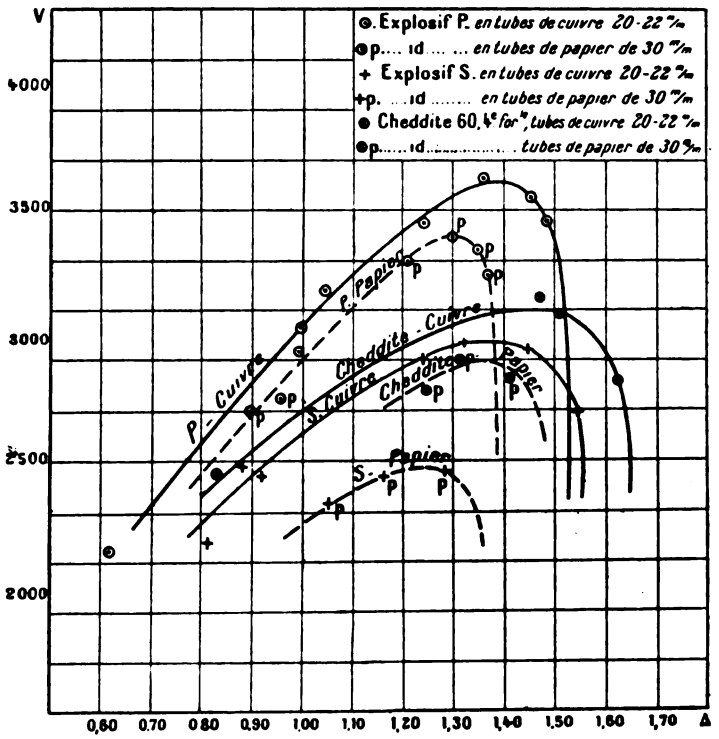

FIG. 97. Velocity of Detonation of Cheddites

Composition	P or O4	S	No. 60
Potassium Chlorate . . .	90	—	80
Sodium Chlorate	—	89	—
Paraffine	10	11	—
Castor Oil	—	—	6
Mononitronaphthalene . . .	—	—	12
Picric Acid	—	—	2

and which are renewed each time. The piston is purposely made heavy so that it may not move appreciably before it has received the full force of the blow. The crushing of the copper cylinder *e* is proportional to the area of the base of the cartridge, but, as has recently been found by Kast, it is only affected by the height of the cartridge up to a limit.[2] Thus with picric acid,

[1] Kast, *Spreng- und Zündstoffe*, p. 1031.

[2] *S.S.*, 1913, p. 89.

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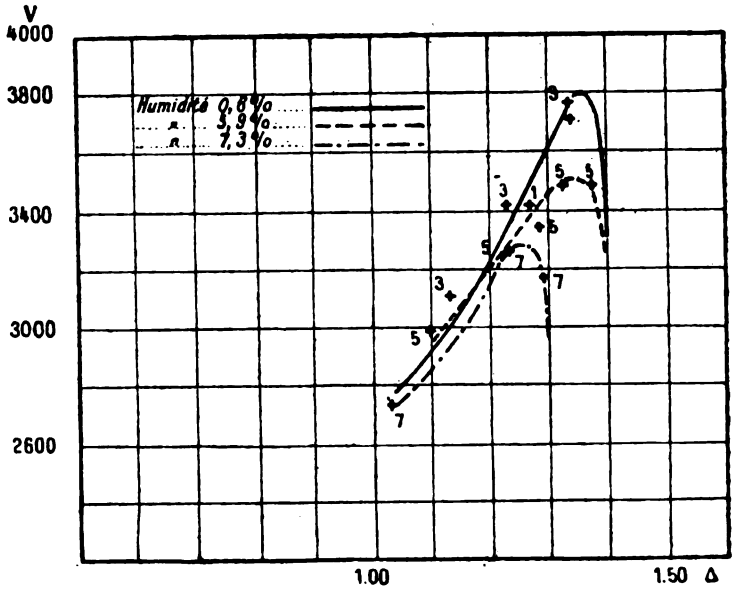
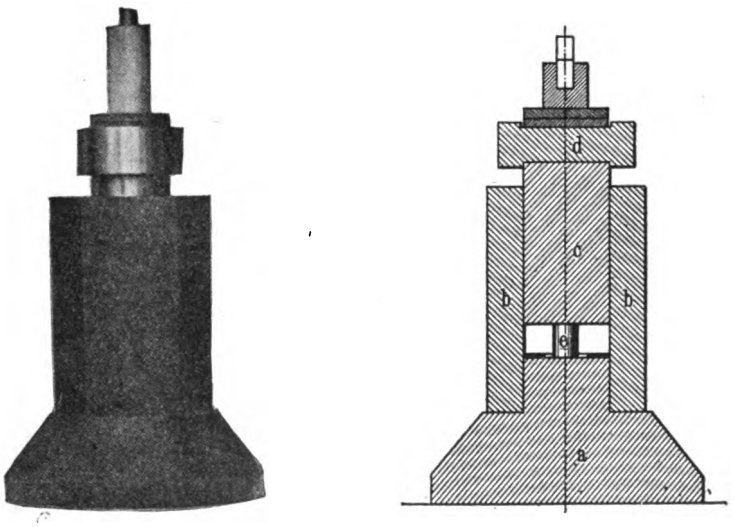


FIG. 98. Effect of Moisture on the Velocity of Detonation of Explosive N3

Sodium Nitrate	58
Trinitronaphthalene	27
Ammonium Nitrate	15



View Section

FIG. 99. Br sance Meter

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specific gravity 1·5, compressed into cartridges 21 mm. in diameter but of varying lengths, the following compressions were obtained :

Detonator	Cartridges		Compression mm.
	Weight gr.	Length mm.	
2 g. . . .	15·0	30·8	3·49
,, . . .	20	40·9	3·65
,, . . .	25	51·2	3·79
,, . . .	30	61·5	3·85
,, . . .	35	69·3	4·09
,, . . .	40	78·0	3·96
3 g. . . .	30	61·4	3·79
,, . . .	34·8	71·9	4·02
,, . . .	40	80·2	4·04
,, . . .	45	90·8	3·81

Similar results were obtained with trinitro-toluene and Macarite.

When the length of the cartridge is not much greater than the diameter, the wave front is curved, and consequently does not all arrive at the bottom end of the cartridge at the same instant ; this spreading of the blow over an interval of time apparently causes a weakening of the effect. To obtain comparable results, the cartridges of different explosives should be made up of the same dimensions, or preferably of sufficient length to get the maximum effect. Unfortunately, most of the experiments that have been carried out in the past have been made up with a fixed weight of explosive, 10 or 15 g., and so short that the maximum effect has not been attained. The result is that the relative effect of the denser explosives appears less than it should, as the cartridges are shorter.

It has been suggested above (p. 391) that the brisance is proportional to the product E.U.D, where E is the kinetic energy of unit weight of the explosive, and U is the velocity of detonation, and D the density. Unfortunately, the only published tests that have been carried out with sufficiently long cartridges are those by Kast on the three explosives already mentioned :

Explosive	Density D	Velocity of Detonation U	Relative Potential Energy E	$\frac{E.U.D}{10000}$	Compression of Copper
Picric acid . . .	1·5	7000	100	105	4·05
Trinitro-toluene . .	1·5	6600	94	93	3·59
Macarite . . .	2·6	4500	104	122	4·38

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The relative potential energy of trinitro-toluene is obtained from the Trauzl tests carried out by Bichel,[1] and that of Macarite from the pamphlet of the inventors, who call it "force spécifique." The relative brisance of the three explosives is as follows, that of picric acid being taken as 100 :

	By calculation E.U.D	By direct measurement Compression of copper
Picric acid	100	.. 100
Trinitro-toluene . . .	89	.. 89
Macarite	116	.. 108

Kast also measured the compression produced by various explosives at different densities using cartridges weighing 15 g. each, 21 mm. in diameter and having a hole for the detonator 15 mm. deep and 9·2 mm. diameter :

Explosive	Density	Compression	Velocity of detonation
Tetranitro-methylaniline . .	1·42	3·57	—
	1·53	3·91	7145
	1·59	3·94	7160
Picric acid	1·34	2·81	6160
	1·46	3·34	6700
	1·53	3·55	7000
	1·60	3·88	7100
Trinitro-chlorbenzene . . .	1·66	3·36	6800
Hexanitro-diphenylamine . .	1·32	3·32	—
Trinitro-benzene	1·35	2·93	6300
	1·51	3·39	6900
	1·60	3·35	7000
Trinitro-cresol	1·37	2·78	—
	1·46	2·99	—
	1·63	3·31	6850
Trinitro-toluene	1·34	2·80	5940
	1·45	2·93	6400
	1·50	3·13	6590
	1·60	3·13	6680
Dinitro-benzene	0·93	1·61	—
Macarite	2·65	2·52	about 4600
	2·75	2·86	4700

[1] *Marine Rundschau*, Nov. 1905.

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In considering the relation between the results of the crusher test and the velocity of detonation, account must be taken of the conditions under which the test is carried out: the explosive is unconfined, and the effect is measured before the velocity has had time to settle down to its steady value. The value of the crusher test lies in the fact that it affords in a simple manner a measure of the practical effect that may be expected when the explosives are used for the hasty demolition of structures for military purposes.

Other tests for brisance.

The brisance of different explosives can also be compared by detonating them on plates or discs of lead or steel and comparing the cavities formed. Unfortunately, this method does not lend itself readily to measurements, but the results are frequently instructive.[1] It is much used for testing detonators, quite small lead plates being used.

F. Martin measures the brisance of detonators by observing their effect on small sensitive flames.[2]

Tests under water.

Explosives for use in submarine mines have been tested under water, advantage being taken of the incompressibility of water, and its consequent power of transmitting the effect of the explosion to a distance. Blochmann devised a dynamometer which registers the pressure as a function of the time [3] similarly to the pressure gauges of Petavel and Bichel. The curve thus obtained (Fig. 100) has two distinct maxima separated by an interval of about 0·05 second when there is 1 metre of water between the explosive and the dynamometer. Bichel also has carried out experiments with this apparatus,[4] and is of opinion that the first maximum is a measure of the percussive force of the explosive, and the second of the gas pressure. The following are his results; the first series was carried out with equal weights, and the second with equal volumes:

Explosive	Density	Charge	Height of 1st maximum	Height of 2nd maximum
Trinitro-toluene	1·55	500 g.	28·0	29·5 m.m.
Gun-cotton, dry	1·25	,,	27·5	30·0 m.m.
Ammon-carbonite . . .	1·19	,,	17·0	19·3 m.m.
Gun-cotton, dry	1·20	450 c.c.	31·5	35·4 m.m.
,, 10 per cent. water .	1·20	,,	31·0	35·0 m.m.
Picric acid	1·44	,,	31·0	30·0 m.m.
Trinitro-toluene	1·61	,,	39·9	37·8 m.m.

[1] *See* Bichel, *Testing Explosives*, p. 61; *Marine Rundschau*, Nov. 1905; *A. and E.*, 1906, p. 21; also Hess, *Ang.* 1904, p. 553.

[2] *C.Z.* 37, 1913, p. 90.

[3] *Marine Rundschau*, 1898, No. 2.

[4] *Marine Rundschau*, Nov. 1905; *A. and E.*, 1906, p. 21.

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Cronquist [1] has measured the effect of explosives under water by the action on hollow lead cylinders placed some distance away. These have a central hole, which is closed by means of a brass plug: the specific gravity is determined before and after, and from the difference the pressure is calculated.

FIG. 100. Diagram from Dynamometer under Water.

It was found that with a slow explosive, such as gunpowder, the effect, as might be expected, varies inversely with the square of the distance, but with more brisant explosives it falls off much more rapidly, and with picric acid it is nearly inversely proportional to the fourth power of the distance. For instance, when the distance is increased from 4 to 5·5 metres, the effect, if proportional inversely to the square, would fall to 53 per cent. of its former value. Those actually measured were:

Gunpowder	50–55 per cent.
Gel. VIII.	46–48 ,,
Extra dynamite . . .	40 ,,
Bellite	36 ,,
Gun-cotton	30 ,,
Picric acid	28 ,,

[1] *Sixth Int. Cong. Appl. Chem.*, vol. 2.

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CHAPTER XXIX

IGNITION AND DETONATION

Definition of explosion : Development of explosion : Initiators : Fulminates and azides : Manufacture of caps, etc. : Precautions : Wet process : Dry process : Drying : Drum method : Jelly-bag method : Charging : Pressing : Varnishing : Inspection : Official definition : Testing caps : Percussion primers : Friction tubes : Electric tubes : Igniters : Detonators or blasting caps : Packing : Precautions : Disposal of waste : Testing detonators

Definition of explosion.

An explosive is a solid or liquid substance or mixture of substances which is liable, on the application of heat or a blow to a small portion of the mass, to be converted in a very short interval of time into other more stable substances largely or entirely gaseous.

The temperature of the products is always very high in consequence of the liberation of a considerable amount of heat in the chemical changes that take place.

The above definition excludes many objects which are capable of exploding, but are not explosives in the ordinary meaning of the word, and consequently do not form the subject matter of this book. Gaseous explosive mixtures, for instance, are of enormous technical importance, but are not the products of the explosives industry.

Development of explosion.

In the last chapter it was shown how explosions vary in power and violence. In this one the development of the explosive wave will be discussed and the methods of initiating it. When an explosive, such as a smokeless powder, is "ignited," it burns from the surface inwards in parallel layers with a velocity which depends upon the pressure, but even under several thousand atmospheres never exceeds a few metres per second : the ignition is communicated from layer to layer by the heat generated. On the other hand, when an explosive is detonated the wave of detonation proceeds apparently through the mass of unaltered explosive with a velocity of several thousand metres per second, changing the material as it proceeds : in this case the explosion is communicated by pressure, but possibly this pressure acts by suddenly raising the temperature by compression.

A mechanical mixture of different substances, no one of which is able to explode by itself, such as black powder, cannot be made to detonate properly, because the chemical change can only take place at the points where the

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oxidizer and the combustible substances are in contact. Even under the most severe conditions as to pressure and initial shock the velocity of explosion does not exceed about 300 metres per second. But if saltpetre be replaced by potassium chlorate, which can be detonated, even when not mixed with combustibles, the case is quite altered and a high explosive is obtained, the velocity of detonation of which is several thousand metres per second.

When gunpowder is ignited it burns very rapidly, even if unconfined. The porosity of even highly compressed powder facilitates the spread of the flame. The rate of burning is affected comparatively little by pressure : hence the use of fine grain powder to ignite cannon cartridges.

Nitric esters, such as nitro-glycerine and gun-cotton, do not attain a very high rate of combustion when unconfined, even if in a state of fine division. This is apparently due to the fact that under these conditions the decomposition takes a different course from that which is followed when they are exploded in a confined space : the nitrogen is mostly set free in the form of nitric oxide or peroxide, and the heat liberated is very much less.

Initiators.

In the early days gunpowder was always ignited by means of a flame ; later sparks from a flint and steel were utilized to light a priming of mealed powder, which communicated the flame to the charge. Not until the nineteenth century was use made of small quantities of sensitive explosives that could be ignited by a blow. It was the discovery of fulminate of mercury, which rendered this possible, and this substance is still an essential constituent of most cap compositions. When used by itself in sufficient quantity to ignite gunpowder with certainty, the fulminate produces such a sudden pressure that it deforms the cap. Therefore it is mixed with other substances which diminish violence and at the same time increase the heat of explosion. Saltpetre, sulphur and mealed powder were formerly added, but now potassium chlorate and sulphide of antimony are usually employed ; some cap compositions contain all these constituents. Ground glass has also been used to increase sensitiveness, but it is not necessary when fulminate is present, and being chemically inactive it, of course, diminishes the power of the cap. For use with smokeless powders, cap composition should not contain more than about 20 per cent. of fulminate of mercury, otherwise the pressure generated will be too high. Numerous attempts have been made to devise cap compositions containing no fulminate, such as a mixture of chlorate of potash and sulpho-cyanide of lead, but although a considerable degree of success has apparently been achieved, such compositions have not come into general use, probably on account of the difficulty in attaining the uniformity necessary with mixtures containing no one constituent which is both sensitive and explosive, especially as mixing by grinding is from the nature of the mixture impossible.

In the case of ordnance the conditions are somewhat different from those

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in small-arms : a larger quantity of material can be used, and a greater amount of force is available. Compositions can therefore be used containing no fulminate. They usually consist of potassium chlorate and antimony sulphide, together with a little sulphur to facilitate ignition and some glass powder to increase sensitiveness. The flash from this is communicated to some black powder, which in turn ignites the cartridge.

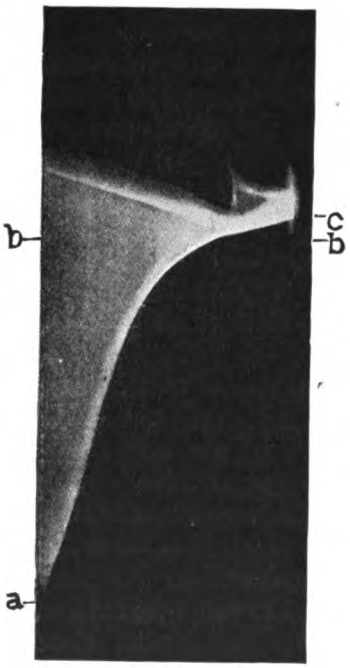

FIG. 101. Explosion of Mixture of Cyanogen and Oxygen (Dixon)

For the ignition of powders in fire-arms, heat only is required ; for the detonation of high explosives, on the other hand, a very sudden and intense blow is necessary, and this can only be obtained by means of an explosive which itself detonates with a velocity of several thousand metres per second. Detonators are always fired by means of heat supplied either by a burning fuse, or by a priming ignited by an electric current. When a light is applied to fulminate, at first it only burns with a velocity of about 10 metres per second, but the reaction becomes more and more rapid, and within an interval of time, which is probably not more than $\frac{1}{3000}$th of a second, detonation sets in. The transformation of combustion into detonation has been shown experimentally in the case of explosive gas mixtures, and may be clearly seen in the photograph by Dixon reproduced in Fig. 101. This is a reproduction of a photograph taken on a film travelling rapidly in the direction, *b* to *a*. The object photographed was a glass tube, *ac*, containing a mixture of cyanogen and oxygen. The mixture was ignited at the end, *a*, by means of an electric spark ; ignition proceeded with a moderate and fairly uniform velocity for a short time, then the velocity increased, and at the point, *b*, detonation suddenly set in, and then the detonation wave travelled on to the end, *c*, of the tube with a uniform velocity of several thousand metres per second. The detonation set in so violently that there travelled back from the point, *b*, a wave of compression, which was sufficiently powerful to raise the gas again to incandescence. This wave, which is called the " wave of retonation," moves with a velocity slightly less than that of the wave of detonation. From the end, *c*, of the tube the wave of detonation also is reflected back with somewhat lower velocity.

When a sensitive solid explosive, such as fulminate of mercury, is ignited, it probably behaves in much the same way as a gaseous mixture, but the

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transition from burning to detonation is so rapid, and takes place in such a minute space, that it cannot be followed.

An explosive can be used successfully to initiate detonation only if, after ignition, it detonates within a very short interval, and before any considerable quantity has burnt away. That is to say, the distance, *ab*, which in the case of the gas mixture shown in Fig. 101 amounts to several decimetres, must not be more than a few millimetres, or preferably only a fraction of a millimetre. Recent developments in the manufacture of detonators are due to no one more than to Professor L. Wöhler, who has investigated a number of different explosives with regard to this property. He calls it initial velocity,[1] but it is really acceleration and not velocity. In 1907 he published, together with O. Matter, the results of experiments with a number of sensitive explosives[2] The following were some of the figures obtained :

	Density	Relative power in lead block c.c.	Temperature of ignition
Silver azide	3·38	22·6	290°
Mercury fulminate . . .	3·37	25·6	190°
Chlorato-trimercuraldehyde . .	3·00	15·3	130°
Diazobenzene nitrate . . .	1·46	43·1	90°
Nitrogen sulphide	2·11	39·2	190°
Sodium fulminate	1·65	14·9	150°
Basic mercury nitro-methane . .	2·45	7·5	160°

The power was determined in each case with 2 g. compressed into a detonator tube and fired with safety fuse in a lead block considerably smaller than that used for blasting explosives. Similar tubes were also fired standing on small lead plates : the results were in the order of the above list, silver azide perforating the plate most. Of all these explosives silver azide, mercury fulminate and the aldehyde are the only ones that have a sufficiently high acceleration to be of any use as initiators of detonation, and the azide is much more effective than fulminate of mercury. The aldehyde is too sensitive to be of practical use. It was made evident that the capacity to initiate detonation, depends little, if at all, on the sensitiveness either to heat or to mechanical influences. The effectiveness of the substances as initiators was ascertained by first placing a quantity (usually 1 g.) of an insensitive explosive in a tube, gently pressing it down, then putting in a small quantity of the initiator and pressing the whole down with a pressure of 2000 kg. per sq. cm. It was finally fired

[1] Anfangsgeschwindigkeit, *see Ang.*, 1911, pp. 2089–2099.
[2] *S.S.*, 1907, pp. 181, 203, 244, and 265.

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on a lead plate to see if the detonation of the explosive was complete. By varying the quantity of initiator the minimum quantity was ascertained which would bring about detonation under these conditions :

Explosive	Minimum weight of initiator (grammes)	
	Silver azide	Mercury fulminate
Gun-cotton	—	·2
Picric acid	·024	·25
Trinitro-resorcin . . .	·08	·3
Trinitro-cresol . . .	·05	·3
Trinitro-benzoic acid . .	·1	·25
Trinitro-benzene . . .	·05	·25
Trinitro-toluene . . .	·05	·25
Trinitro-xylene . . .	·025	·4

Detonators constructed on this principle are now manufactured extensively. At first picric acid was used in combination with fulminate, but now trinitro-toluene or tetranitro-methylaniline are employed. The latter is the most effective, but it is more expensive than trinitro-toluene and somewhat more sensitive. The firm of Allendorff, for instance, makes a No. 8 detonator containing 0·7 g. trinitro-toluene covered with 0·5 g. of fulminate of mercury. This is fully equal to the usual charge of 2 g. fulminate and chlorate.[1] Unfortunately, fulminate is liable to deteriorate on keeping, and with such a small quantity as 0·5 g. the decomposition of a small proportion is likely to be more harmful than when there is a larger quantity present originally. Lheure [2] found that detonators containing picric acid and fulminate were more irregular than those charged with fulminate alone.

Fulminates and azides.

In a later communication [3] Wöhler discusses other substances that may be used as initiators of detonation, especially the various azides. Those of silver, copper and lead have such high auto-acceleration that they develop their full effect even when quite unconfined, and the same applies to nitrogen iodide, which, however, is so sensitive that it is exploded by a touch. Fulminate of mercury does not produce its full effect when quite unconfined, but a thin copper capsule provides sufficient confinement. The difference in the rates of acceleration is shown by exploding a small quantity in a test-tube : fulminate of mercury does not injure the tube, whereas fulminate of silver pierces it, and azide of silver shatters it to a thousand fragments. These

[1] *S.S.*, 1907, p. 5.

[2] *P. et S.*, vol. xii., p. 134.

[3] *Ang.*, 1911, p. 2089. *See also* further communication by Wöhler and Martin, *S.S.*, 1914, p. 242 ; *Ang.*, 1914, vol. i., p. 335.

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results are in accordance with the results of tests carried out to ascertain the minimum amounts required to detonate trinitro-toluene:

Mercury falminate	·25 g.
Silver fulminate	·15 g.
Lead azide	·05 g.
Silver azide	·02 g.

Lead azide is now used as a substitute for fulminate for the manufacture of detonators. As long ago as 1893 experiments with the azides of silver, lead and mercury were started at Spandau by the Prussian Government, and met with considerable success, but they were stopped in consequence of a man being killed by an explosion. Lead azide is considerably less sensitive than fulminate of mercury, provided that it be in a fine state of division, but unlike the fulminate it can be obtained in crystals of a considerable size, and these are much less stable. It is indeed a general rule that the sensitiveness to shock increases with the size of the crystals. The material is evidently in a state of great strain; the strong double refraction of the crystals of all these "initiators" confirms this. Mercuric azide, for instance, when in crystals measuring 0·6 to 0·9 mm., is not much more sensitive than mercuric fulminate, but if the crystals are allowed to grow to 3 mm. diameter, it is liable to explode spontaneously even under water. Lead azide is made by the double decomposition of sodium azide and lead acetate, and the size of the crystals of the precipitated lead azide depend on the temperature. In 1910 in Germany a man was killed in a factory by the explosion of some lead azide under water, and there have been other fatal accidents.[1]

The azides are not so brisant as the fulminates. It is possible to combine the high acceleration of the former with the brisance of the latter by the use of a combined charge. Thus fulminate of mercury to which a centigramme or less of lead azide has been added is even more effective in detonating trinitro-toluene than the azide itself. Diazo-benzene nitrate also, which is of but little use by itself as an initiator of detonation, becomes very effective by the addition of a centigramme of lead azide.

Wöhler has determined the sensitiveness of many of these substances both to temperature and to the falling weight:

	500 g. weight falling mm.	Temperature of ignition.
Mercury fulminate	75–100	200°
Siver fulminate	140	200°
Sodium fulminate	over 320	150°
Mercuric azide (crystals ·6–·9 mm.)	65	200–210°
,, azide (,, 3 mm.)	0	200–210°
Mercurous azide	200	300°

[1] *S.S.*, 1911, p. 417.

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	500 gr. weight falling mm.	Temperature of ignition
Silver azide	310	300°
Cupric azide	0	—
Cuprous azide	260	200–210°
Lead azide (finely divided)	260	340–350°
„ azide (moderate crystals)	130	340–350°
Basic lead azide	280	380°
„ cupric azide	315	245°

Wöhler suggests that the basic azides may be used in cap compositions instead of fulminate. They have comparatively low accelerations, and consequently are not so liable to deform the cap or give high pressures in the fire-arm.

One of the disadvantages of fulminate of mercury is that it deteriorates on storage, especially if the temperature be high or the atmosphere moist. In Austria there is an official regulation that detonators are to be stored over fused calcium chloride.[1] Different lots of fulminate differ considerably as to their liability to deteriorate, but this matter does not appear to have been studied very much. Lead azide seems to be much more permanent. This is clearly shown by the photographs by Wöhler reproduced in Fig. 102; originally, of course, detonators of both descriptions perforated the lead plates.

A B

FIG. 102. Effect of Detonators on Lead Plates after keeping in Moist Atmosphere 200 Days

A. Charged with Lead Azide.
B. Charged with Mercury Fulminate and Potassium Chlorate.

The lead azide is generally used in conjunction with Tetryl (tetranitro-methyl-aniline) or trinitrotoluene. The latter is put into the copper capsule first and pressed down, then the azide, and over that a disc of copper with a central perforation, and the pressing is repeated. The disc, which is also used in fulminate composite detonators, is to prevent the upper layer of explosive falling out and also to protect it from moisture.[2]

Both in the design and the use of detonators it should be borne in mind that the greatest effect is produced in the direction in which the wave of detonation is travelling. The most effective part is therefore the closed end of the detonator. Care should be taken that nothing intervenes between the end of the detonator and the explosive. The end should not be filled up with a small plug of putty, for instance, and when inserting the detonator into the cartridge of explosive it should be pressed well in, so that there may be no air space beyond the end.

[1] *See S.S.*, 1909, p. 38.

[2] Neitzel, *S.S.*, 1913, p. 171.

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Manufacture of Caps, Detonators, etc.

Special precautions must be observed when dealing with the very sensitive substances used for charging caps, detonators and other igniters; there is far more danger of explosion than there is with other explosives. The danger is diminished by restricting the quantities that are allowed to be present in any one building. As the amount of explosive in each cap or detonator is small, this restriction does not interfere seriously with the work. The total quantities dealt with are not small, however, for it is estimated that 100 tons of fulminate of mercury are made in Germany every year, and a single factory in Great Britain manufactures more than double this quantity. The various constituents, before mixing, are sifted through fine sieves to remove all gross gritty particles. The fulminate and the explosive mixtures are kept and transported in small boxes of papier mâché or other soft smooth material. In those buildings where quantities of a pound or more may be present *en masse*, the floors should be covered with linoleum or other soft stuff, and the workers should all wear felt slippers or only socks. The greatest cleanliness should be observed. **Precautions.**

The mixing and drying operations are specially dangerous. The mixing of the composition was at one time done in a very simple way by placing the ingredients on a piece of paper and then stirring them with a goose feather, or by lifting first one corner of the paper and then another. Under these conditions it was never possible to protect the worker adequately, and with such very sensitive material there is always great danger of an explosion. Now the mixing is either carried out wet, or it is done in a "jelly-bag."

The wet process of mixing has been described in detail by Hagen: [1] its essential feature is that the explosive is kept wet until the mixing is complete. As the ingredients tend to separate from one another when wet, even more than when dry, in consequence of the differences in their densities, it is necessary to incorporate with them a binding material, usually gum arabic, although Alden uses gelatine. The fulminate and other constituents are mixed together by hand in a basin with just sufficient of a 6 to 7 per cent. solution of gum arabic to wet it thoroughly. Then the mixture is granulated by pressing it through first a sieve with about 6 meshes to the inch, and then one with 15 meshes. By official order these sieves must be of hair or silk. The granulated composition is dried at a temperature of 30° to 35°; then it is sifted, and that portion is selected which passes a 50-mesh sieve and is retained by a 120: this constitutes about 60 per cent.; the remainder is returned to the granulating house, where it is moistened again and mixed with fresh composition. **Wet process.**

Only just enough water should be used thoroughly to moisten the mixture,

[1] *S.S.*, 1911, pp. 201, 224, 243, 265, 283, and 308.

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so that when it is worked it is formed into a uniform thick mud. This is not very easy, and in spite of precautions some of the composition is liable to get dry. If it be too wet, the liquid will carry away some of the potassium chlorate and other soluble constituents. Alden overcomes this difficulty by adding alcohol, which reprecipitates the chlorate, and also the gelatine which carries down with it all matter in suspension, and so clarifies the liquid. The cap composition for the Austrian military rifle is made as follows: 540 g. of finely ground and sifted potassium chlorate are placed in a basin, and 284 c.c. of a 3 per cent. solution of gelatine are added, and they are stirred together until all lumps have been broken up. Then 210 g. of wet fulminate, containing 15 per cent. of water, are stirred in, and finally 435 g. of antimony sulphide and 140 g. glass powder. Then 500 g. of 95 to 96 per cent. spirit are poured in, and the liquid is allowed to settle. The composition is filtered off on a fine double cloth, allowed to drain, pressed down, and then squeezed out by two girls, who twist round the two ends of the cloth.

The wet process suffers under the disadvantage that the workers are constantly manipulating considerable quantities of composition, and, although the material is kept wet most of the time, ignitions are not uncommon.

At one time wet composition was loaded directly into the caps by some makers. This method had the advantage that dry composition did not have to be manipulated in bulk at all. But when it dried in the cap it formed a hard mass, which was sometimes exceptionally sensitive and led to accidents.[1] Friction tubes for ordnance are still sometimes loaded by this method, but the compositions for these generally contain no fulminate.

Dry process. Fulminate, which is always stored wet until actually required, must, of course, be dried before mixing by the dry process.

Drying. The drying is carried out in an isolated building, where the wet fulminate is spread out on soft fabric. The building is heated by means of hot-water pipes to a temperature of 30° to 35°. The drying occupies only a few hours, as the fulminate is not at all hygroscopic. Then the building is allowed to cool down: on no account should the fulminate be touched until it is quite cold, as its sensitiveness increases with the temperature.

The drying is also carried out sometimes in vacuum drying ovens.

Drum method. In some Continental factories the mixing is carried out in drums of papier mâché 40 cm. in diameter and 15 cm. thick.[2] Two of these rotate within a strong enclosure. In the first all the constituents, with the exception of the fulminate, are mixed together, soft rubber balls being added to the charge to assist the mixing. The axle is turned for a few minutes by hand from behind a protecting wall. Then the contents of the drum are emptied out through a funnel and a coarse sieve, which retains the rubber balls but allows the composition to pass through. The fulminate is then added to this, and the

[1] *See S.R.*, No. 113, para. 13.

[2] *See* Knoll, *Knallquecksilber*, p. 153.

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mixing is repeated in the same way in the other drum which, however, contains no rubber balls. Each charge is about 250 g.

The " jelly-bag " method originated in France, but is now generally adopted in Great Britain also. The plant is shown in Fig. 103. The various constituents, amounting altogether to ½ lb. to 2 lb., are put into the silk bag, the fulminate last. Then the workman retires behind the screen and works the lever for about three minutes to effect the mixing. Then the lever is drawn right down, so that the bag is turned inside out, and the mixed composition falls through the leather funnel into a small box standing on the bracket just below it. Explosions have occurred in this plant occasionally, but have only done very slight damage, and the workman has always escaped injury. The machine is generally arranged, however, so that he is further removed from the explosive than is shown in the figure. Mechanical power is now often substituted for hand labour, as the mixing is then more uniform. Instead of the rubber rings soft rubber balls are used ; they are placed loose in the bag, and are separated afterwards by means of a coarse sieve. Over the top of the plant a cotton sheet should be suspended to make sure that nothing can fall into the bag. **Jelly-bag method.**

The ingredients are not mixed together very intimately, but this is no disadvantage, as the violence of the caps is thus diminished.

The charging and pressing of the caps is performed in machines such as those made by Greenwood and Batley, of Leeds. The capsules are made of copper, more rarely of brass ; they are punched out of sheet metal and pressed to the required shape. The permissible variations in dimensions are very small. They are then lacquered with varnish to prevent actual contact between the composition and the metal. The capsules are filled into a plate or " hand " which has a large number of depressions, each just large enough to take a capsule ; there may be as many as 1000 of these depressions, 40 rows of 25 each. **Charging.**

The charging machine consists essentially of several brass or bronze plates, each perforated with a number of holes corresponding to the depressions in the " hand." The holes in the top plate are just large enough to take the quantity of composition required for one cap.

A little more than enough composition to fill all the caps is placed on the plate, and then with a piece of soft cloth or rubber the worker passes it over the plate and so fills all the holes. As the charge of each cap is only 0·3 to 0·6 grain (0·02 to 0·04 g.), the total quantity of explosive is not much more than 40 g., and the explosion of this would not do very serious damage, provided it be not allowed to spread to more composition. The stock of composition must therefore be kept in a safe place at some little distance. By a slight movement of the second plate each charge is now caused to fall into its cap. This movement is produced by means of a long rod, so that the worker is not near the explosive.

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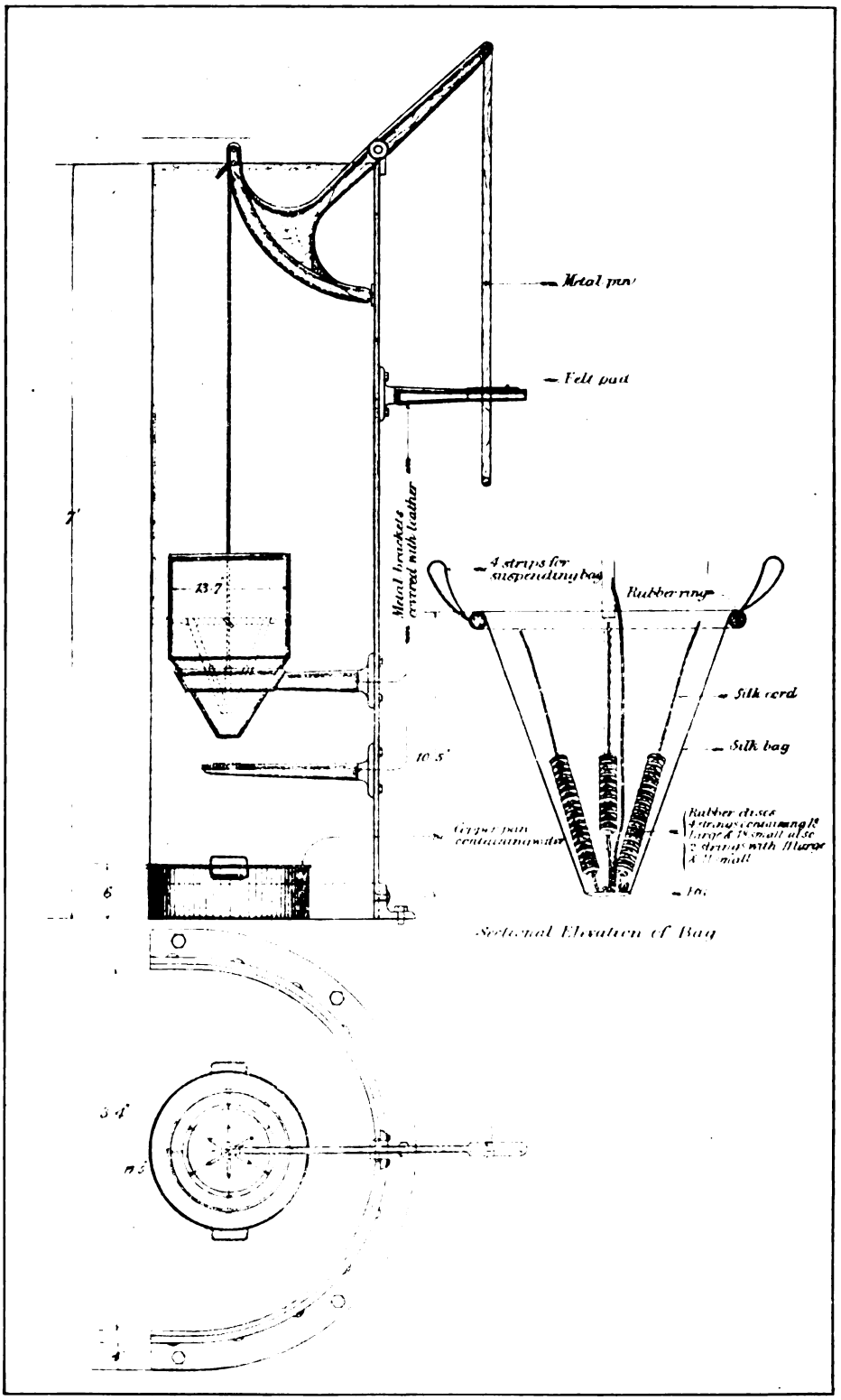

FIG. 103. Jelly-bag Plant for Mixing Fulminate Compositions

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The charges have next to be pressed. This is carried out in a machine which has a row of pistons, that are made to descend on to the caps. Each piston is weighted with a separate weight, connected to it through a system of levers so that not more than a certain pressure, say 2 cwt., can be exerted on each cap. When one row of caps has been pressed, the hand moves forward automatically so as to bring the next row under the pistons.[1] **Pressing.**

Any loose composition is now removed by exposing the caps to a mild blast of air in a special cupboard, which should be so arranged that the composition carried away by the air is caused to fall into a pan of water. Then the composition is varnished. This operation is performed in an apparatus which has a number of pins projecting vertically downwards from a movable horizontal plate, one pin for each cap in a hand. The plate is brought down until the pins dip into a shallow trough containing a solution of shellac in spirit. Then it is raised again and a hand of caps is slipped under it, and it is brought down again so that a small drop of the varnish is deposited in each cap. The caps are then removed from the hand and dried at a gentle heat to remove the alcohol, and finally they are drummed or "rumbled" in order to clean them. They are then ready to insert into the cartridge cases. **Varnishing.**

The composition in each cap is frequently covered over with a small disc of tin-foil. This is essential if the caps are not to be loaded into cartridge cases in the same factory, because otherwise there is danger of some of the composition escaping. Not only would this make the caps unreliable, but the loose composition would render them liable to explode in bulk. There are two ways in which the tin-foil may be introduced. One way is to stamp the foil from a sheet straight into the caps in a special machine. In the other method a lot of discs of foil are placed in a tray, down on to which is brought a plate bearing a number of little vertical tubes. A vacuum is applied to these so that each picks up a disc. The hand is then slipped under it, the plate is again brought down, the vacuum is released, and so a piece of foil is introduced into each cap. The caps are then pressed again and varnished.

An alternative scheme of working is as follows : [2] The composition receives a preliminary pressing, the excess of composition is blown off, and foil having still moist varnish on its under side, is stamped straight into the caps, which then receive their final pressing. This method is used when the composition has binding material incorporated with it by the wet process. Finally the caps are drummed and sifted so as to remove all loose composition.

During and between all the operations careful supervision is necessary to make sure that no defective caps pass through the process, for a missfire **Inspection.**

[1] *See also* Hagen, *S.S.*, 1912, pp. 277, 297, 322, 343, 367, 388, 411, 431, and 449.

[2] *See* Knoll, *Knallquecksilber.*

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is always annoying and may be dangerous, and irregularity in the charges of the caps leads to unevenness in the ballistics of the cartridges.

When used in rifles foiled caps are liable to cause fouling of the rifling, unless there be sufficient excess of oxygen in the composition to oxidize the metal of the foil completely. The effect produced by the cap depends upon many circumstances: the nature of the powder, the nature and quantity of the composition, and the way in which it has been mixed and pressed, the shape and size of the cap chamber and the anvil on to which the cap is knocked by the blow of the hammer or bolt, and the size of the fire-holes through which the products of the cap impinge on to the powder. All these factors combine together to cause the more or less rapid ignition of the powder, and consequently it is not possible to specify any one composition as the best under all circumstances. Mixtures of fulminate, potassium chlorate and antimony sulphide are used almost exclusively, although there are serious objections to all three substances. The fulminate is dangerous and expensive; it deteriorates on keeping, especially when moist, and on explosion it gives metallic mercury, which injures the brass of the cartridge case, so that it cannot be used again for the same purpose. The antimony from the sulphide is also very injurious to the brass, and the chlorate forms chlorides, which cause the barrel to rust, unless it is cleaned thoroughly after firing. There are many other mixtures that can be employed, but apparently none of them is sufficiently reliable and satisfactory for general use. Of the oxidizing agents available, saltpetre cannot be used because it is too hygroscopic, but it is not easy to see why barium nitrate cannot be substituted for potassium chlorate. As combustibles the following have been used or proposed: lead ferrocyanide, copper ammonium thiosulphate,[1] lead sulphocyanide, mercury sulphocyanide, metallic aluminium, sulphur. As substitutes for the fulminate, Wöhler has proposed the use of basic azides. Use has, however, sometimes been made of mixtures containing no substance which is explosive by itself. The United States, for instance, use for their small-arms a mixture of potassium chlorate 47·2 per cent., antimony sulphide 30·8 per cent., sulphur 22 per cent.

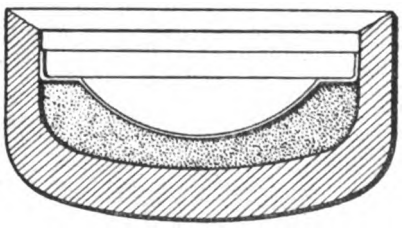

FIG. 104. Percussion Cap for Cartridge of Mannlicher Rifle
Magnified 10 Diameters

The following are some fulminate compositions that are used:

[1] *See* Herz, *S.S.*, 1912, p. 284.

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	Austrian (Hagen)		English Small-Arms	
	Small-arm	Shot-gun	Gunpowder	Cordite
Mercury fulminate	13·7	33·9	37·5	19·0
Potassium chlorate	41·5	21·6	37·5	33·3
Antimony sulphide	33·4	—	25·0	42·9
Glass powder	10·7	43·2	—	—
Gelatine	0·7	1·3	—	—
Sulphur	—	—	—	2·4
Mealed powder	—	—	—	2·4

The proportion of glass in the second mixture is very large; in England compositions for shot-gun caps often contain no glass powder.

The products of explosion of a composition should contain a considerable proportion of non-volatile solids, so that a high temperature may be produced combined with a low pressure.

Official definition.

According to the ruling of H.M. Chief Inspector of Explosives, percussion caps must be of such strength and construction that the ignition of one will not ignite the others. Each cap must not contain more than 0·5 grain of composition (0·032 g.), which must be protected by a coating of tin-foil or other material approved by the Inspector, and it must not contain the anvil. If the proportion of fulminate in the composition does not exceed 25 per cent., the charge may be increased to 0·6 grain (0·039 g.). If these conditions are not fulfilled, the cap is considered to be a detonator, and must be packed and stored accordingly.

Testing caps.

An old and simple method of testing percussion caps consists in flashing them against a piece of white paper from a fixed distance and comparing the marks made. This only affords a rough indication of the uniformity of manufacture. The pressure generated may be measured in the apparatus made by Cogswell and Harrison.[1] The cartridge case is screwed down on to a hollow steel rod, inside which works a piston. The other end of this piston bears against a small lead crusher. The cap is fired by dropping a weight from a known distance on to a striker. The pressure generated by the cap is then communicated to the piston, and the consequent diminution in the length of the lead cylinder affords a measure of the pressure. The same instrument can also be used to determine the energy of blow necessary to fire the caps properly. Brownsdon [2] has given a number of methods for examining caps. The flash may be photographed, and the results are often instructive. The volume of gas generated can be measured by firing the cap in a closed chamber,

[1] *See* Guttmann, *Manufacture*, vol. ii., p. 369.

[2] *J.S.C.I.*, 1905, p. 381.

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and at the same time an indication of the amount of heat liberated can be obtained by having a delicate thermometer projecting into the chamber, and reading the rise of temperature. The time of flash was estimated by flashing caps towards a rotating disc pierced with a number of holes, behind which was a camera focussed on to the disc. From the length of the marks made by the illuminated holes, and the known velocity of rotation, the duration of the flash could be calculated : it was estimated to be about 1/3000th of a second.

The methods have been further developed by Borland.[1] He estimates the length and duration of flash by firing a cap in front of a slit behind which a photographic plate is revolved, thus obtaining a V-shaped image. The heat generated he measures by firing against a thermocouple, instead of a thermometer. The temperature of the flash was measured directly, by means of an optical pyrometer, from the intensity of light in a selected portion of the spectrum. The temperatures recorded ranged from 1150° to 1520°, but when the caps were coated with aluminium powder temperatures of 1570° and 1690° were obtained. The temperatures as calculated with the aid of Mallard and Le Chatelier's specific heats were about twice as high, but in these calculations no allowance was made for heat lost by radiation and conduction and by the work done in the expansion of the gases. The results obtained with the optical pyrometer were found to be unaffected by considerable variations in the quantity of composition in the cap. An indication of the temperature can also be obtained by exposing portions of the same photographic plate to the flashes from different caps, and comparing the densities of the developed plates in a Chapman-Jones plate tester.

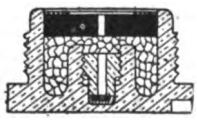

FIG. 105.
Percussion Primer for Quick-firing Ammunition

Percussion primers.

For the percussion primers of quick-firing gun ammunition the conditions are somewhat different. First, there is more force available, and consequently the composition need not be so sensitive ; and, secondly, the flash is not required to ignite the powder charge directly, but is first communicated to a small quantity of small grain black powder, which in turn ignites the cartridge ; consequently these caps do not require to be so uniform in their effects as those used for small-arms. The compositions generally contain no fulminate, but consist principally of potassium chlorate and antimony sulphide. Fig. 105 shows the construction of a German percussion primer. The percussion cap is held in place by the screwed anvil, through which there is a perforation permitting the flash to ignite some fine grain powder. Over this there is a pellet of compressed powder, also with a central perforation, held in position by a disc of shirting and a brass plate with fire-hole, held

[1] *J.S.C.I.*, 1906, p. 241.

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down by the turned-over edge of the primer. After it has been assembled the primer is varnished.

Friction tubes.

The friction tubes for igniting gun cartridges that are not enclosed in metal cases are constructed on much the same principle, except that the pellet of composition is ignited by the friction of a bar or wire pulled or pushed through it, instead of by the blow of a striker or bolt. As the tube has to be inserted through a hole in the wall of the gun, it must be several inches long. The tube is filled with powder grains or pellets, which carry the flash well into the chamber of the gun. At the top of the tube is the pellet of composition, which is made of a mixture similar to that used for the percussion primers. Hagen gives the following figures for the composition used in friction tubes :

Potassium chlorate . . .	66·2 per cent.
Antimony sulphide . . .	33·1 „
Gum arabic	0·7 „

Half of the chlorate is only coarsely ground.

Electric tubes.

Naval guns and guns of position are often fired electrically. For this purpose tubes are used in which the friction pellet is replaced by some priming composition, consisting of a mixture of mealed powder and gun-cotton dust, or other easily ignited material. Through this passes a short piece of fine platinum wire, the two ends of which are connected with two copper wires, which can be joined to the poles of a battery. The general construction of the electric tube resembles that of an electric detonator, except that the fulminate is replaced by black powder, and the tube is more solidly constructed. All igniting tubes, whether friction or electric, must be so designed that the powder gases cannot blow out through the outer end.

Igniters.

The flame from the tube does not suffice, however, to ignite the cartridge, which consequently has to be provided with an igniter. This generally consists of fine grain black powder contained in a bag or pocket covering the end of the cartridge. The quantity is generally from $\frac{1}{2}$ to 2 per cent. of the weight of the smokeless powder. There are various objections to the use of black powder for this purpose, and attempts have been made to find some other material that may be substituted for it. One objection is that this priming considerably increases the amount of smoke that is formed when the charge is fired. For guns of small calibre ungelatinized gun-cotton in the form of yarn is sometimes used, but no priming gives such regular ballistics as the black powder, especially in the big guns.

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Detonators or Blasting Caps

Detonators are manufactured in much the same way as percussion caps, but in consequence of the greater violence of the charge, and the far greater quantity in each, much more stringent precautions must be taken for the protection of the workers. The capsules are drawn copper tubes without joint, closed at one end. Of these 100 are placed in holes in a plate or "jig," which is often made of ebonite, the holes being lined with brass to prevent deformation. The capsules should fit the holes well but not tightly. Over this jig is placed another plate with the same number of holes, the thickness of the plate being such that each hole will just take the requisite quantity of fulminate loosely packed to charge one detonator. This upper plate slides over the jig so that the holes can be brought opposite to those in the latter. At first, however, the upper plate is placed so that the holes do not communicate. Dry fulminate, or fulminate mixture, is placed on the top plate in quantity rather more than sufficient to fill the 100 detonators, and is then gently swept into the holes; then the upper plate is slid over so that the fulminate falls into the capsules. These operations are carried out from behind a strong shield by means of rods passing through it, so that if the fulminate explodes, the worker will not be injured. The upper plate is then removed, and the surface of the jig is gently wiped down with a damp cloth to remove any loose explosive. The jig is then taken to the press, which has 100 small pistons fitting closely but not tightly into the capsules. The pressure applied to the fulminate is usually about 250 kg. per sq. cm. or 50 to 60 kg. on each detonator, which compresses the explosive to a density of about 2·2. If the density be raised by increasing the compression, the fulminate becomes less sensitive, and consequently a larger quantity burns away before detonation sets in, so that although the brisance of the detonating portion is greater, the effectiveness of the whole detonator may be less. The variation of the density and of the power with the pressure were determined by Wöhler and Matter by exploding charges of 2 g. in lead blocks : [1]

Pressure kg/cm²	Density	Trauzl test c.c.
100	1·92	30·6
400	2·56	28·5
800	2·98	26·0
1200	3·21	25·6
1600	3·23	25·4
2000	3·36	25·6

There is, of course, no direct connexion between the results of the Trauzl test and the effectiveness of a detonator, but the figures show how increase of

[1] *S.S.*, 1907, p. 245.

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density can have a bad effect. After pressing, the detonators are removed from the jig either by tipping it over into a pan containing sawdust, or by pushing them out from below. Then they are drummed, or "rumbled," and sifted, to remove the sawdust and all loose fulminate. During these operations also, the workers must be protected by strong shields.

Finally they are packed in tin boxes, each of which contains not more than 100. The boxes must be lined with paper or similar material, and there must be a pad of felt, cotton wool or other soft stuff against the ends of the detonators. The spaces between the detonators and in their open ends are filled with sawdust. These boxes are then packed in an outer package. If the number of detonators within the outer package exceed 1000, there must be a double outer package with a space of 3 inches everywhere between the two. If the number exceed 5000 the outer package must have handles to assist the moving. The maximum allowed in one outer package is 10,000.[1] **Packing.**

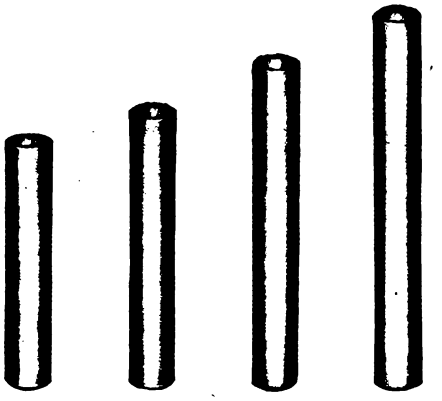

FIG. 106. Detonators

Detonators of different strengths are distinguished by numbers, which are the same in all countries :

No	Usual external dimensions of tube		Charge g.
	Length mm.	Diam. mm.	
1	16	5·5	0·3
2	22	5·5	0·4
3	26	5·5	0·54
4	28	6	0·65
5	30–32	6	0·8
6	35	6	1·0
7	40–45	6	1·5
8	50–55	6–7	2·0
9	—	—	2·5
10	—	—	3·0

The numbers in common use are 5 to 8.

[1] Explosives Act.

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As regards the composition of the charge, in France fulminate of mercury only is used, but in other countries it is generally mixed with chlorate of potash up to 25 per cent. The total energy is thereby increased, as the carbon is converted into dioxide instead of monoxide :

$$Hg(CNO)_2 = Hg + N_2 + 2CO$$
$$3Hg(CNO)_2 + 2KClO_3 = 3Hg + 3N_2 + 6CO_2 + 2KCl.$$

The theoretical proportion for complete oxidation is 77·7 of fulminate to 22·3 of chlorate : in practice 15 to 20 per cent. of chlorate is generally used. A further advantage of the addition of the chlorate is that it causes the charge to run better in the loading machines. On the other hand it diminishes the acceleration of explosion and the density, and causes the detonators to deteriorate somewhat more rapidly ; the results also are not so regular.[1] In some works the fulminate is pulverized by grinding it wet with a wooden pestle. By this the mechanical sensitiveness is decreased and the acceleration is increased, and so a double advantage is obtained, but the grinding operation is a troublesome and somewhat dangerous one. Detonators with composite charges are made up so that they shall be as strong as those of the corresponding number containing only a mixture of fulminate and chlorate. The following are some of the composite charges that are in use :

No.	Trinitro-toluene or tetranitro-methylaniline	Fulminate of mercury
5	0·3 g.	0·3 g.
6	0·4 g.	0·4 g.
7	0·75 g.	0·5 g.
8	0·9 g.	0·5 g.

Precautions. In spite of every care explosions occur from time to time with such sensitive substances as fulminate, and in order to prevent widespread disaster it is necessary to restrict the quantities that may be present in any one place, and to separate the different working places and operations, so that an explosion at one spot may not cause other explosions. The German regulations lay down the following limits :

	Limit of explosive
1. Drying house and magazine for dry mixture	
(*a*) With a minimum distance of 10 m.	50 kg.
(*b*) „ „ „ 15 m.	75 „
(*c*) Vacuum drying oven	0·5 „
2. Charge in press for wet mercury fulminate and wet composition	3 „

[1] *P. et S.*, vol. 12, p. 134.

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	Limit of explosive	
3. Mixing, corning, or sifting house for dry composition	10	kg.
4. Charge of the mixing, corning, or sifting appliances for dry composition	5	,,
5. Charging compartment for detonators	1	,,
6. Charging compartment for percussion caps		
(*a*) Machine charging with loading machine separate	500	g.
(*b*) ,, ,, with loading machine not separate	100	,,
(*c*) Hand charging with separate filling room	100	,,
(*d*) ,, ,, without separate filling room	30	,,
(*e*) ,, ,, protected with shield	500	,,
(*f*) Contents of transport case	1500	,,
7. Store for detonators	1000	kg.
8. Concrete magazine for detonators	3000	,,

The greatest care should be taken not only to remove from the range of any possible explosion, any composition or finished caps or detonators not actually required for the work in hand, but also to clean up at frequent intervals any composition that may be spilt or blown about. Accidents have been caused by workpeople treading on spilt composition or detonators.

Disposal of waste.

The disposal of waste composition and articles containing it is a matter of importance and some difficulty. The German regulations lay down that mother liquors from the fulminate, as well as all wash waters and residues, must be deprived of their explosibility before they are run to waste. It is recommended that this be done by boiling the strongly acid liquid for four or five hours in vessels of earthenware or wood by means of steam-coils or live steam. Alkali should not be added, as it is liable to lead to the formation of dangerous intermediate compounds. Moistened waste composition may be destroyed in the same way, or it may be stirred with a mixture of 3 parts of hydrochloric acid and 1 part of nitric acid until the fulminate of mercury has been entirely destroyed. When the vessel is emptied, the solid residue should be collected on a filter cloth, or the liquid should be drawn off by means of a cock so placed that only liquid can escape by it. The liquid should be neutralized with lime before it is run to waste. The solid residue should be tested as to its explosibility, and the boiling should be continued until it is inexplosive.

Filter cloths, sponges, etc., should be kept under water and put into a fire whilst still wet. Sawdust, which has been in contact with composition, should be destroyed in the same way.

Waste detonators and caps are to be kept in sawdust and destroyed by burning at least once a week. In the case of detonators, the burning place should be protected.

The English Inspectors of Explosives, on the other hand, recommend that detonators be destroyed by dissolving them entirely in a mixture of 2 parts concentrated hydrochloric acid and 1 part water.

Loose composition or fulminate can be destroyed very rapidly by stirring

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it with a solution of sodium thiosulphate in excess, but the liquid should be kept acid by the addition of hydrochloric acid. Large accumulations of explosive waste should be avoided.

If large numbers of waste detonators have to be destroyed, they may be tied together in bundles of 50 or 100 with an electric detonator in the middle, and the whole bundle can be detonated at one time. The explosion should be carried out in a suitable pit, and the men should be properly protected.

Testing detonators.

The strengths of detonators can be compared by firing them in contact with lead plates, on which they are either laid or stood vertically.[1] Or they may be detonated in small lead blocks, as in the Trauzl test. Another method is to ascertain their power of detonating an insensitive explosive; by means of the Trauzl test or by determining its velocity of detonation it is possible to make certain whether the detonation has been complete. The U.S. Bureau of Mines has adopted a test in which the effect of the detonator on a 4-inch wire nail is measured:[2] the detonator is attached to the nail so that the bottom end is $1\frac{3}{4}$ inches from the face of the head of the nail. The nail and the detonator are parallel to one another and separated from one another by two 22-gauge (0·025 inch) copper wires that are wrapped round the detonator. The nail is fastened to the detonator by a single strand of the same wire round the middle of the detonator. When the detonator is fired the nail is bent and projected upwards: the angle to which it is bent is a measure of the strength of the detonator. The nails should, of course, be uniform in quality and dimensions. F. Martin compares the brisance of detonators by observing their effects on sensitive flames.[3]

[1] *See* Fig. 102.

[2] *See Bureau of Mines Bulletin,* No. 59; "Investigations of Detonators and Electric Detonators."

[3] *C. Z.*, vol. xxxvii, 1913, p. 90.

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PART IX

SOME SPECIAL EXPLOSIVES, ETC.

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CHAPTER XXX

FUSES

Safety fuse : Igniter fuse : Miner's squibs : Quills, etc. : Quick-match : Instantaneous fuse : Slow-match : Detonating fuses : Electric fuses : Mechanical fuses : Shell fuses

FOR the ignition of the detonator or, in the case of blasting explosives of the black powder class, for the direct ignition of the charge, a fuse of one sort or another is used. This is a device by which a flame is communicated to the detonator or charge either after an interval of time, or by an operation conducted at a distance. In either case the shot firer is not exposed to the effects of the explosion.

Safety fuse.

Safety fuse is made or "spun" by allowing fine grain black powder to flow down from a hopper into an inverted cone, in the apex of which there is a small hole. Down the outside of this cone some ten threads, usually of jute, are drawn from reels, through holes drilled in the flange at the base. Below and just clear of the apex of the cone is a thick metal disc, through which the threads pass with the stream of powder in the middle. Then the whole cord passes through a tightening tube. At the same time the frame supporting the reels is rotated so that the thin column of powder is enclosed in a spiral tube. Lower down in the same machine is another similar frame supporting other reels, usually seven in number, and this is rotated in the opposite direction, so that the fuse is doubly wound or "countered." The fuse is then wound on to a drum, on which it is transported to other buildings, where it undergoes further operations, such as winding with tape and impregnating with waterproofing material. The spinning operation must be carried out with the usual precautions required in manufacturing operations with explosives. The floors must be kept clean, and the operatives, usually girls, must wear special clothing without pockets. The hoppers containing the powder should be situated in a loft above the actual spinning-room, so that in the event of an ignition the workers have time to escape before the powder explodes.[1] For descriptions and illustrations of some of the machinery used in the various operations of manufacture, *see* Neumann, *S.S.*, 1910, pp. 87, 107, 130, 148, and 168.

[1] *See S.R.*, Nos. 140 and 178.

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A great many varieties of safety fuse are made, differing principally in the number and character of the layers of covering material, and in the waterproofing applied, if any. In England it is sold in coils of 24 feet, but in America they are 25 or 50 feet long, and on the Continent 10 metres (about 33 feet). In Germany the fuse is coloured to distinguish the different manufacturers one from another, but in England a further distinction is made by varying the colouring of the different varieties.

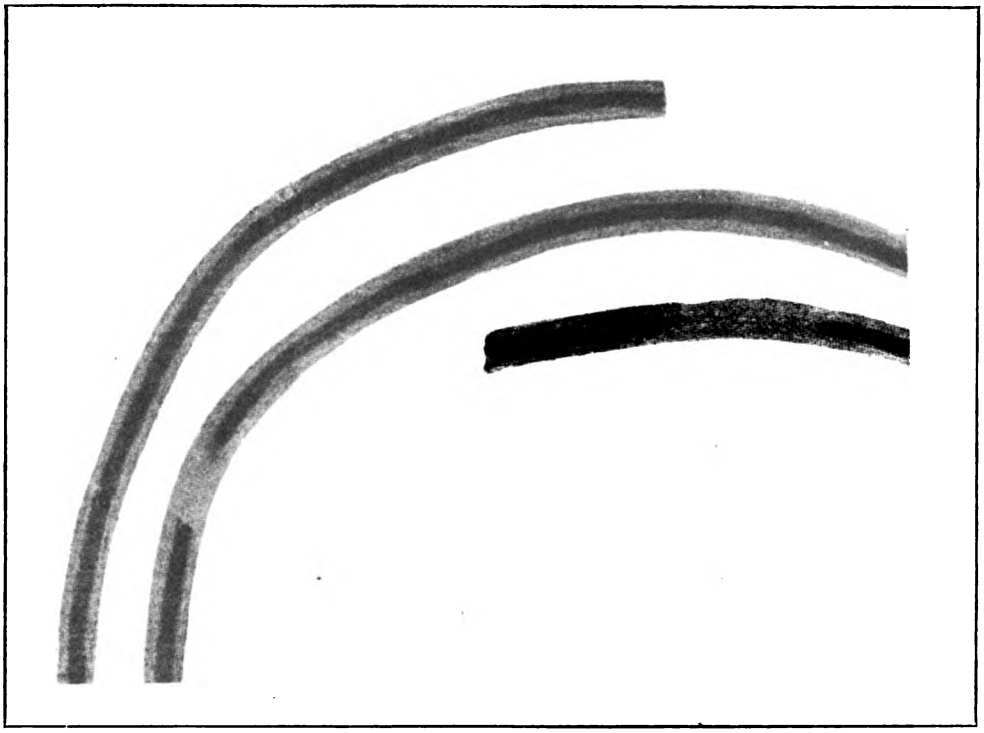

Fig. 107. Safety Fuse under X-rays

Rate of burning.

Regularity in burning is the first requisite of safety fuse: usually it is made to burn in the open at the rate of about 30 seconds per foot or 100 seconds per metre. Sometimes a fuse will fail altogether on account of an interruption of the powder core. Hake pointed out [1] that such interruptions can be detected by examining the fuse under the X-rays (*see* Fig. 107). The rate of burning is usually measured in the open, but unfortunately it is much affected by the pressure to which the fuse is subjected: if tamped hard with plastic clay the rate of burning may be increased to three or even five times the normal rate; [2]

[1] *J.S.C.I.*, 1903, p. 1224.

[2] *See S.S.*, 1908, p. 348.

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with porous and less plastic tamping materials, such as dry clay or sand, the powder gases can escape as they are formed, and the rate of burning is only slightly increased. Snelling and Cope[1] found that under an air pressure of one atmosphere the rate of burning was increased about 30 per cent. Exposure to a high temperature makes the fuse burn more slowly, especially if it be coated with waterproofing material which becomes soft under this treatment. If stored for a long time in a damp place, the burning is retarded and may be interrupted altogether.

Waterproof fuse must be capable of burning properly after a longer or shorter immersion in water, and colliery fuse must not give off laterally any sparks that could ignite coal-damp. The following are the tests applied officially to fuse imported into the Transvaal :[2]

(*a*) A piece of fuse 4 yards long is immersed in water except 6 inches at either end, and for twenty minutes is submitted to a pressure of 10 lb. per square inch. Then one end is lit. (Fuse often fails under this test.)

(*b*) A piece 2 yards long is pressed flat between pieces of wood in a vice, and is burnt whilst submitted to this pressure.

(*c*) A number of pieces 2 yards long are taken from different coils, bound together at one end and ignited simultaneously. The difference in the time of burning must not be more than 5 per cent.

(*d*) Pieces 2 yards long are bent double and put into iron tubes $1\frac{1}{2}$ inches in diameter, and burnt in the air and also in water : the former to see if ignition is communicated laterally, and the latter as a test for waterproofing.

(*e*) The shower of sparks from the end of a fuse must be able to ignite another piece of fuse at a distance of 1 inch. For this test the two pieces of fuse are inserted into the opposite ends of a piece of glass tube.

When submitted to any of these tests the variation from the guaranteed rate of burning must not exceed 10 per cent.

Igniter fuse.

In fiery coal-mines the use of a naked flame to ignite the safety fuse would be dangerous. Consequently devices are made for lighting the fuse in a closed space. The third schedule of the Explosives in Coal-Mines Order of May 21, 1912, lays down that : " The fuse shall consist of a core of gunpowder, protected by not less than three coverings of thread or by not less than two coverings of thread and one of tape or gutta-percha. The fuse shall be of such quality that the time of burning of the fuse shall not vary more than 10 seconds above or below the rate of 90 seconds for every yard of fuse. The fuse shall be ignited by means of an igniter contained in a tube which when attached to the fuse forms a completely closed chamber." In the second schedule of the Order of February 21, 1910, the following description is given of Bickford's Igniter Fuse : " . . . consisting of a tube of tinned iron or steel,

[1] *Bureau of Mines Technical Paper* 6, Washington, 1912.
[2] *S.S.*, 1910, p. 55.

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closed at one end, and containing a mixture of chlorate of potassium and sugar pressed into a pellet not exceeding 100 milligrammes in weight, in close contact with a hermetically sealed glass capsule containing concentrated sulphuric acid ; a length of specially prepared colliery fuse, as is hereinafter defined, being fitted into the open end of the tube and the joint being cemented by a tape bearing the ' Crown ' and letter ' P.' . . .

" The said fuse shall consist of a core of gunpowder in weight not exceeding 6 grammes per metre, traversed by two threads and enclosed by :

" (1) A layer of jute yarn ; (2) a laver of jute yarn laid in the contrary

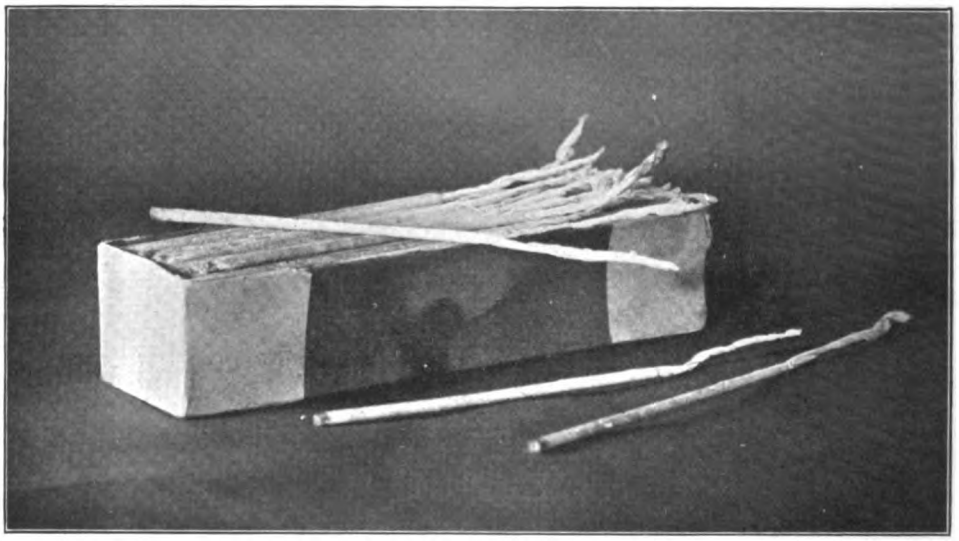

Fig. 108. Miners' Squibs

(From *Bureau of Mines Bulletin*, No. 17)

direction ; (3) a layer of tape ; (4) a layer of tape laid in the contrary direction ; (5) a layer of jute yarn secured by a suitable varnish. (The three outer layers being specially treated with a fireproofing composition.)"

For fireproofing, such substances as ammonium phosphate and sodium tungstate may be used. For fuse of this sort jute or hemp is better than cotton, because it is less liable to smoulder.

The special tests to which igniter fuse is subjected were laid down in *A.R.*, 1906, Appendix O, p. 143 :

(1) Five lengths of 12 inches of the fuse to be ignited. This must show no visible incandescence anywhere even when fanned.

(2) Five lengths of 12 feet of the fuse with the lighters attached to be wound round a 2-inch cylinder, straightened, and fired by means of the recog-

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nized firing arrangement, the whole, except not more than 6 inches of the cut end, being in a highly explosive atmosphere of coal-gas and air.

(3) Test No. 2 to be repeated with twenty igniters and shorter lengths of fuse not previously wound round a cylinder, to test lighting arrangement only.

The fuse is considered to have failed if it causes an ignition in either 2 or 3.

More primitive igniting arrangements are still used in some mines and quarries, where stringent regulations are not in force. One device is the miner's squib (Fig. 108), which consists of a tapering paper tube about 7 inches

Miner's squib.

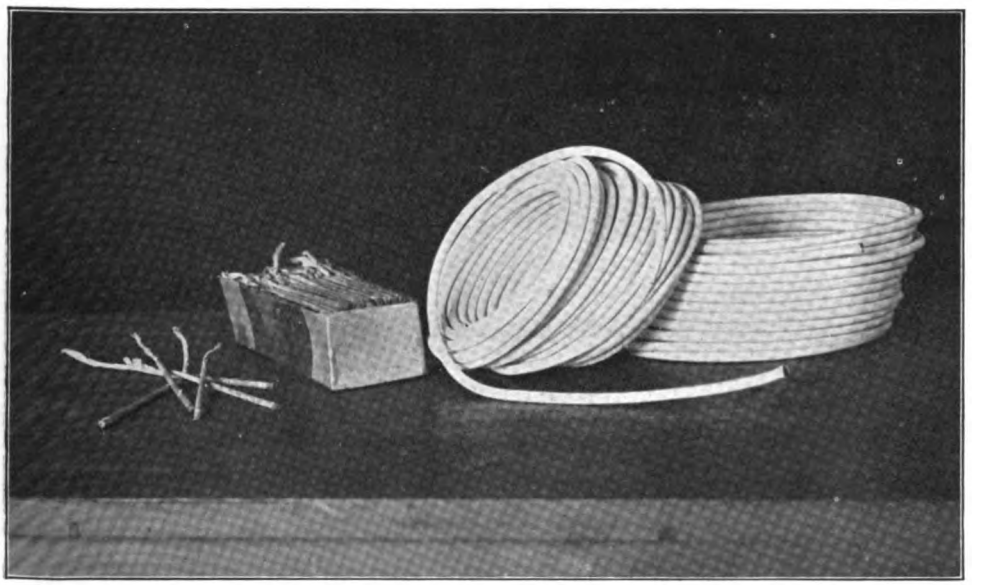

FIG. 109. Squibs and Safety Fuse

long, filled with fine gunpowder. One end of the paper tube is treated with chemicals so as to form a slow-match, which when ignited takes so long to burn that the miner has time to reach a place of safety before the explosion. When used, the squib is placed in the needle hole or blasting barrel through the tamping with the match end of the squib outward. When the match is lit, the fire burns slowly until it reaches the powder core; then the squib darts forward like a rocket, leaving a trail of flame behind, which spurts out of the needle hole, and the fire continues burning along the squib until it bursts out at the other end of the tube and so ignites the charge.

Another simple device is a quill filled with powder and joined to a piece of slow-match. Strips of blasting gelatine are also used. These are all very objectionable and dangerous. In South Africa "Cheesa sticks" are used,

Quills, etc.

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which consist of sticks of cordite coated with ammonium oxalate and shellac. They have recently been authorized in England.

Quick-match. Quick-match was formerly used for igniting charges both in military and civil blasting; it is still used in making up fireworks, etc. It is made of cotton wick boiled with a solution of mealed powder and gum, and afterwards, before it is quite dry, dusted over with mealed powder. Unenclosed it burns at the rate of a foot in about four seconds, but if enclosed in a tube it burns much more rapidly.

Instantaneous fuse. Instantaneous fuse consists of several strands of quick-match enclosed in a wrapping of waterproof tape: its speed is from 100 to 300 feet per second. Formerly it was much used in extensive blasting operations, where a number of charges had to be fired simultaneously, but it has now been superseded by electric detonators and detonating fuses. It was fired by means of a percussion cap in a special pistol.

Slow-match. Slow-match is made by boiling loose hemp cords in a dilute solution of saltpetre; it smoulders away at the rate of a foot in several hours; it is used when a long delay is required.

Detonating fuses. Many attempts have been made to produce a fuse still more rapid by filling it with an explosive capable of being detonated, but it is only of recent years that real success has been achieved. As long ago as 1879 a detonating fuse was introduced into the French army: it was made by filling a lead tube with pulverulent nitro-hydro-cellulose and then drawing it out until it had a diameter of 4 mm. A metre weighed about 88 g. and contained 5 g. of the gun-cotton; it detonated at the rate of about 4000 metres per second. It was somewhat sensitive to blows, and does not seem ever to have come into general use. Attempts to make detonating fuse filled similarly with other powdered explosives were also unsuccessful. In Austria General Hess introduced a fuse constructed on the same principles as instantaneous fuse, except that the threads were impregnated with a mixture or paste of fulminate of mercury, glycerine and water, but more recently the fulminate has been phlegmatized with 20 per cent. of hard paraffin instead. The fuse thus produced (Knallzündschnur M.03) is stated to be satisfactory.[1] Only a very violent blow will cause it to explode; if ignited, it merely burns away, but if heated so much that the paraffin melts and separates from the fulminate, it becomes dangerous. When fired with a 2 g. detonator it detonates at the rate of 5000 to 6000 metres per second.

In Italy fuse is made by filling a lead tube with finely powdered ballistite. It can be used either as a detonating or slow-burning fuse. In order to enable it to burn under water some black powder is mixed with the ballistite. In spite of statements to the contrary, this fuse must deteriorate rapidly on keeping.[2] When fired with a 1 gr. detonator it

[1] *See S.S.*, 1907, p. 173.

[2] *See* Neumann, *S.S.*, 1910, p. 172.

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detonates at the rate of 5000 metres per second; when lit, 1 metre burns in four minutes.

In France detonating fuse has been made by filling tin tubing with powdered picric acid, and then drawing it out. A great improvement was effected by Lheure, who for this substituted trinitro-toluene in a lead pipe. The explosive is melted and drawn into the lead tube by vacuum, and when cold the tube is drawn out to a diameter of about 4 mm., using special precautions to ensure uniformity. Other explosives, which are insensitive, easily melted and not plastic, could be used, such as tetranitro-methyl-aniline or trinitro-benzene, but they are more expensive. Trinitro-toluene is therefore used by the manufacturers, Davey, Bickford, Smith et Cie., of Rouen. This fuse has been used successfully for some considerable operations, such as the destruction of a canal tunnel at Hollebeck in Belgium, where 2125 charges were fired simultaneously, amounting to 3250 kg. of explosive. The principal use of detonating fuse is for military demolitions, in which the simultaneous explosion of a number of charges is of importance, as also are simplicity and ease of application. For some purposes, such as the destruction of wire entanglements and iron fences, the fuse can be used by itself. For use in ordinary mines and quarries its high price is somewhat prohibitive, but it is contended by Lheure [1] that it can be used in coal-mines without increasing the danger, and that its use leads to a saving of 20 per cent. of the explosive (grisounite). The saving is apparently due to this very insensitive explosive not being detonated entirely by an ordinary detonator, whereas with a piece of detonating fuse running the whole length of the charge detonation was complete, or at any rate more nearly so. For the detonation of insensitive explosives, Brunswig [2] advocates that advantage should be taken of the fact that at the point where two waves of detonation meet in a piece of fuse detonated from both ends, the effect is very much greater, but it is not apparent how this property could be utilized in ordinary practice. This fuse is utilized for the measurement of the velocity of detonation of explosives (*see* p. 393).

Another French firm makes flattened tubes filled with tetranitro-methyl-aniline, and for work in coal-mines, with this substance mixed with nitro-guanidine.[3]

Electric fuses.

The development of electrical science and industry naturally led to the idea of firing explosives by means of an electric current. Heat generated by a current is utilized to fire a suitably constructed fuse, and this ignites a detonator, which in turn explodes the charge. Much ingenuity has been devoted to the designing of electric fuses, but they may be divided into two main classes: high and low tension fuses. In the former a spark is made to

[1] *Annales des Mines*, 1907 : *S.S.*, 1908, p. 141.
[2] *Eighth Inter. Cong. App. Chem.*, 1912, vol. iv., p. 23.
[3] *See* Chalon, *Explosifs modernes*, 1911, pp. 424–428.

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pass between two metal poles and ignite a priming material such as a tuft of gun-cotton. In the low-tension fuses there is a small bridge of fine wire, generally made of platinum, and this is heated to incandescence by the current, thereby igniting the priming. The fuses now used are nearly always of the

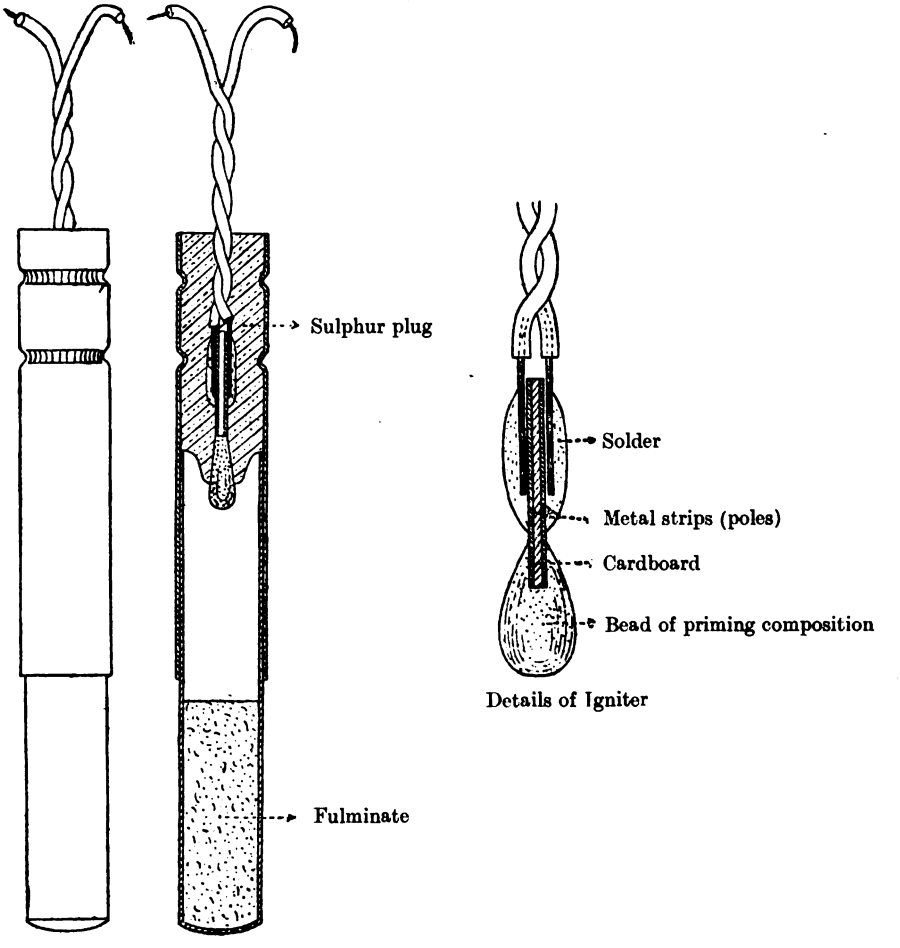

FIG. 110. Electric Detonator

low tension type : one of the advantages that they possess over the other type is that each fuse before use can be tested as to the resistance that it offers to the current, whereas a high tension fuse can only be tested by firing, and so destroying it.

In order to protect the fine wire bridge from fracture it is often embedded in a solid bead of priming composition. As a rule the electric primers are

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attached to the detonators in the factory, and the electric detonators thus made are supplied complete ready for firing. Fig. 110 shows, for instance, the construction of the electric detonators made by the " Fabrik Elektrischer Zünder," in Cologne. The two connecting wires are soldered to two strips of metal foil, which are attached to the opposite sides of a piece of cardboard. For low-tension fuses these strips are connected by a piece of platinum wire, and the whole is dipped into a mixture containing potassium chlorate and antimony sulphide, so as to form a bead like the head of a match, which is then further protected with a covering of shellac and collodion. This is fixed into a tube by means of a plug of molten sulphur, and this tube is slipped over the open end of the detonator capsule, to which it is attached by means of shellac cement.

The wires should not be in contact with very sensitive explosives, such as fulminate, because there is always danger that they may move when handled, and so cause a premature explosion.

The advantages of the electric detonators are that they can be fired from any distance at any moment, and that a number of shots can be fired simultaneously. In blasting a round of holes in hard rock, it is often desired to explode some of the charges before others. This can be done by causing a delay in the firing of the electric detonators for the later shots, as for instance, by introducing a piece of safety fuse between the electric fuse and the detonator. Delay electric detonators are also made in which the whole arrangement is supplied complete. Electric firing suffers under the disadvantage that it is considerably more expensive than firing with safety fuse, but from an analysis of the results obtained during several years in the coal-mine of Heinitz on the Saar, Bulgis finds that though the cost per shot is higher, per ton of coal got it is lower, with electric firing :

		Average cost	
		Per ton coal	Per shot
Safety fuse	1907	0·30*d.*	1·02*d.*
	1908	0·28*d.*	0·92*d.*
Electric	1908	0·28*d.*	1·38*d.*
	1909	0·24*d.*	1·38*d.*

The saving is ascribed to the fact that the electric firing is carried out by special shot-firers, whereas the firing with safety fuse was done by the miners themselves. The miner is inclined to reduce the number of shots to be fired to minimum in consequence of the trouble and annoyance of having to wait for the shot-firer to come round.[1]

[1] *S.S.*, 1908, p. 361 ; 1909, p. 41 ; 1911, pp. 192 and 352.

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Electric fuses are generally made with a resistance of about 1 ohm, and fire with a current of about 0·7 ampère. A few shots can be fired simultaneously by means of a portable battery, but for large numbers this will not give a sufficiently powerful current. They are generally connected up in series with an "exploder," as is shown diagrammatically in Fig. 111. The usual type of exploder consists of a small compound series wound dynamo worked by hand by means of a rod which is pushed down. The voltage is built up rapidly during the stroke until the rod nearly reaches the end of its stroke, when the current is switched into the circuit and fires the shots. Such exploders may be obtained guaranteed to fire 50 or 100 shots simultaneously, but it has been found in the operations on the Panama Canal that there are always some missfires, due to the fact that some of the fuses are more sensitive than others, and they detonate and so destroy the circuit before the less sensitive ones have reached the exploding point.[1] Recourse was therefore had to firing all shots in parallel through a transformer from the main electric supply, and so all trouble from this source was overcome. The reason why there were more failures at Panama, than in ordinary blasting operations, was that very large charges were used at considerable distances apart: holes were drilled to depths of 15 to 60 feet, 12 to 18 feet apart, and each was charged with from 200 to 1000 lb. of dynamite. In ordinary blasting operations the holes are only a few feet apart, and under these conditions, if a detonator fails, the charge is exploded by influence from the other charges, and consequently the danger from unexploded charges is much less; but the effect of the charges fired by influence is comparatively small.

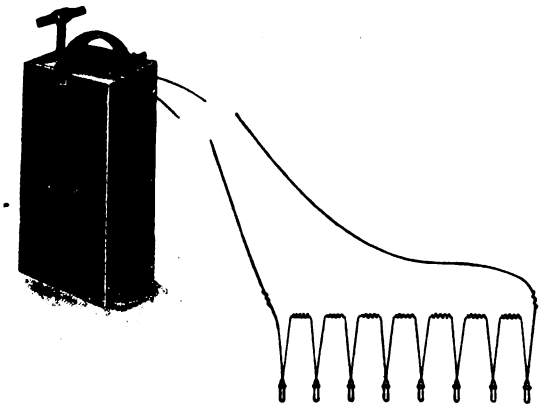

FIG. 111. Electric Exploder and Detonators (Du Pont)

There are also electric fuses specially made to overcome this difficulty by short-circuiting the connecting wires when they are fired. The circuit consequently is not broken at once, but for a small fraction of a second there is an extra powerful current available for firing the less sensitive fuses.[2]

Another defect, that was found to cause failures at Panama, was that the electric detonators were not always quite water-tight, with the result that after immersion in a deep bore-hole for some hours they failed. The failures

[1] *See* Robinson, *Eighth Inter. Cong. App. Chem.*, 1912, vol. iv., p. 85.
[2] *See S.S.*, 1912, p. 459.

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were traced to the action of the sulphur plug on the copper of the shell, whereby the latter was made porous. The detonators in question were of American manufacture.

Mechanical fuses.

Fuses can also be made that are fired by mechanical action as, for instance, by pulling a wire or cord, which releases a striker which is driven by a spring on to a percussion cap. Such devices are but little used, however, except for fuses for firing artillery shell.

Shell-fuses.

There are two main varieties of fuses for shell, namely, percussion and time fuses. The former may be fixed into either the base or the nose of the shell : in either case they generally work on the same simple principle : when the shell strikes an object the sudden retardation either causes a pin to strike a percussion cap or makes the cap fall on to the pin. The flash from the cap ignites some priming composition, and so the ignition is communicated into the interior of the shell proper. The fuses may be provided with a delay arrangement, a short column of combustible matter, which must be burnt through before the flame can reach the shell. This causes the shell to explode only after it has passed through the object struck, the armour plating of a ship, for instance. The fuse must, of course, be so constructed that the cap is not fired by the shock of discharge of the gun, nor by such blows as it may receive in handling and transport. The moving part is therefore held in place, usually by a spring, which can only be overcome by a very severe blow on the nose of the shell. In the case of shell filled with high explosive, the result of a premature detonation in the bore of the gun would be so disastrous, that special safety arrangements are generally introduced. The percussion cap is entirely cut off from the interior of the shell until some disc or bolt has been removed either by the pressure of the powder gases on the base of the shell, or by the centrifugal force caused by the rotation of the shell.[1]

Time fuses are used mostly for shrapnel shell, which is required to burst shortly before it reaches the object shot at. But, as a rule, the fuse also contains a percussion arrangement, so that, if the time mechanism does not function, the shell will still be exploded when it strikes, and so may be of assistance to the artilleryman in gauging the range, even if it does no damage. Time fuses are always fixed to the nose of the shell. The primitive fuses used in the early days were made to ignite by the flame of the powder charge, but now the concussion of the discharge is utilized to fire a percussion cap. Before the flame can reach the bursting charge it has to burn through a lengthy column of comparatively slow-burning composition, generally placed in one or more movable rings. The gunner by twisting one of these round can alter the length of the column to be burnt through, and consequently the range at which the shell will burst. The construction of time and percussion fuses is shown in Figs. 73, 74. Each ring has a circular slot cut in it nearly all the

[1] *See* Exler, *S.S.*, 1909, pp. 63 and 88.

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way round ; it is ignited at one end and the flame travels round until it comes to the hole leading to the next ring or to the priming. Formerly the rings were filled with mealed powder pressed into the slots, but now fine grain gunpowder is generally used, as its time of burning is more regular, a very important consideration. In Austria it is pressed to a density of 1·8 and corned in the usual way ; the grains used measure 0·3 to 0·65 mm. This powder is pressed firmly into the rings.

The time of burning of a fuse with two rings having a total length of 20 cm. filled with gunpowder of the standard composition is about twenty seconds. The range of modern artillery is so great, however, that this is not sufficient in many cases. It is necessary to devise fuses which have a time of burning of some forty seconds without any increase in the relative variation in the time. Ten fuses, burnt under service conditions, should not show an extreme variation of more than 2·5 per cent. of the mean time. An increase in the number of rings adds to the complication and increases the cost, which is already considerable. The powder can be made somewhat slower by increasing the percentage of saltpetre or decreasing that of the charcoal.[1] The addition of graphite has a slight effect in the same direction, and also makes the powder more regular. The addition of vaseline and the substitution of barium nitrate for part of the saltpetre also lengthen the time of burning, but none of these changes makes the powder as slow as is required. The addition of non-volatile inert matter, such as steatite or brick-dust, is not desirable, as it tends to block the passages through which the gases escape. The desired effect can, however, be produced by the use of very slack-burnt charcoal. Dolleczek found that when the yield of charcoal was about 50 per cent., the time of burning was a minimum, namely, about 15 seconds. With a yield of 71 per cent. the time was 25 seconds, and with 80 per cent. 37 seconds. The percentages of carbon in these charcoals were 68, 58, and about 55 per cent. respectively. A brown powder such as was formerly used for ordnance was also tried. The charcoal in this contained only 52 per cent. carbon. The powder by itself would not ignite in the time rings, but when mixed with black powder in various proportions and worked together the mixtures gave times of burning of 40·21 and 33·63 seconds with differences of 1·12 and 0·70 seconds respectively. Promising results were also obtained with slack burnt cork charcoal.

One of the difficulties in the construction of time fuses is to make them sufficiently air-tight, to prevent the absorption of moisture by the powder. A small increase in the percentage of water in the composition contained in the time rings makes them burn considerably more slowly, and if the composition takes up sufficient moisture to become really damp, the fuses become quite unreliable, even when they are dry again. The escape holes are protected with waterproof discs, and the edges of the time rings are coated with

[1] *See* Dolleczek, *S.S.*, 1910, pp. 245 and 273.

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thick lubricant, but even so, care has to be taken in the storage and transport of the fuses in order to maintain them in a serviceable condition. Metal caps are frequently kept fixed over the fuse until it is actually required for use. This question has been dealt with somewhat fully by Gründlich.[1]

In France an entirely different solution of the difficulties connected with the construction of long range time fuses has been worked out. The time composition is not contained in rings, but in a lead tube, which is wound in a spiral inside the fuse. To set the fuse, this tube is stabbed at the appropriate point, whereby the flame is caused to impinge on the priming at the proper time. The tube can, of course, be made of any desired length, and the composition is effectually protected from moisture.[2]

Many attempts have been made to design fuses in which the interval of time is measured off, not by the burning of a composition, but by some mechanical action, such as the passage of air or liquid through an orifice, or in which the space travelled through by the shell is automatically measured by a vane projecting from the nose, which after a certain number of revolutions fires the shell.[3] The only successful fuse of this sort, so far, is that invented by Bäker and taken over and perfected by Krupp, which has a clockwork mechanism driven by a spring. This has been described in detail by Neumann in *S.S.*, 1912, pp. 1 and 25. Unlike the time-ring fuse it is not affected by atmospheric pressure or length of storage, and it is claimed that it is more accurate.

[1] *S.S.*, 1911, pp. 221, 248, 270, and 291.

[2] *See Deutsches Offizierblatt*, 1906, p. 513.

[3] *See* Pangher, *Mittheilungen über Gegenstände des Artillerie- und Geniewesens*, 1906, pp. 38–59 ; *S.S.*, 1906, 340.

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CHAPTER XXXI

SAFETY EXPLOSIVES

Nomenclature : Coal-mine explosions : Testing galleries : In France : In Austria : In Germany : In Belgium : In England : In America : Different systems of testing : Explosive atmospheres : Coal-dust : Influence of size of bore : Dimensions of gallery : Incomplete decomposition : Flames : Effect of alkali salts : Effect of density : Incorporation : Wrappers : Length of the cannon : Stemming : Failure to detonate : Conclusions : Classification

Nomenclature. OBJECTIONS have been raised to the term "safety explosive" on the ground that it is the duty of an explosive to explode, and that therefore it cannot be safe under all circumstances, and that the use of this expression may lead to carelessness in dealing with these materials. On the other hand, it has been contended that the use of the term should be confined to those explosives which are comparatively insensitive to blows and friction, such as ammonium nitrate explosives containing no nitro-glycerine. In German, distinction is drawn between those that are safe in handling (handhabungssichere) and those that are safe for use in coal-mines (schlagwettersichere), and in French it has been proposed to confine the use of the expression "explosifs de sûreté" to the former class, and to call the explosives for dangerous coal-mines "explosifs antigrisouteux." Nevertheless, what is generally understood by a safety explosive is one that has been officially tested and found to be comparatively safe when exploded in the presence of fire-damp (methane).

Coal-mine explosions. In order to prevent mine explosions three important precautions are generally taken : the use of the safety lamp, efficient ventilation of the workings, and the employment of explosives that are not liable to ignite fire-damp. The development of safety explosives and the methods of testing them were briefly reviewed in Chapter III. As the depth and extent of mines has been increased, ventilation has become more and more essential, not only to remove any gas that may escape from the coal, but also to provide a healthy atmosphere for the miners ; but this has greatly increased another source of danger, namely, that from coal-dust. The large volume of air, heated by compression, streaming through the galleries dries the dust produced by the tramping of the men and horses, and this dust is capable of forming an explosive mixture with air. Although not so easily ignited as a mixture of methane and air, it is quite as dangerous, because coal-dust explosions are generally far more exten-

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sive. In December 1907, three explosions occurred in the Pennsylvania coal-field, and in each case practically every man in the mine was killed; the death-roll amounted to 633. In the mine explosion at Courrières, in the North of France, in 1905, about 1100 men lost their lives. There have also been explosions in England and Germany in which several hundred men have been killed. In all these cases the vast extent of the catastrophes is ascribed to the presence of coal-dust. With efficient ventilation it is not possible for fire-damp to be present in explosive proportion except in small isolated localities, but the presence of more or less coal-dust cannot be avoided anywhere. The initial ignition is in many cases probably due to fire-damp, but the explosion is propagated and extended by the dust. The explosive wave is preceded by a rush of air which stirs up the dust and so prepares the way for the explosion. Some sorts of coal give dust which is more dangerous than that from others. Fineness of the dust, a large proportion of volatile matter, and evolution of gas at a low temperature, are factors tending to favour explosion. At the testing stations safety explosives are now tested as to their liability to ignite mixtures of coal-dust with air, or with air and inflammable gas. As a general rule the results obtained are much the same as with mixtures of air and inflammable gas only, but some explosives of the ammonium nitrate class ignite coal-dust more readily than they do gas. Other measures have also been tried for diminishing the danger from coal-dust: watering the roads and galleries in order to lay the dust throughout a mine and make it uninflammable is unfortunately impracticable, although it can generally be adopted in the immediate vicinity of the place where a shot is to be fired. In various testing galleries experiments have been carried out with fine stone-dust, which is found to be able to damp out an explosion: by its application it should be possible to prevent the extension of coal-dust explosions. It has also been suggested by Harger that the air in a mine could be rendered incapable of forming explosive mixtures by diminishing the percentage of oxygen in it, but this theory is not generally accepted, and it is contended that the experimental facts do not bear out Harger's statements.

Testing galleries.

In all the principal countries of Europe, possessing coal-mines, testing galleries have been erected, in which safety explosives can be tested by firing them into an explosive atmosphere.

France.

In France a testing station has been built at Liévin by the coal owners of the Pas de Calais. There is a small gallery 2 square metres in section and 15 metres long for the study of explosives, and a large one 2·8 square metres in section and 300 metres long for the study of coal-dust explosions, etc. The selection of explosives for use in French coal-mines was until recently based on theoretical considerations; the following two conditions had to be satisfied:

(1) Their products of detonation must contain no combustible constituent, such as hydrogen, carbon monoxide, solid carbon, etc.

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(2) Their temperature of detonation, calculated in the prescribed manner, must not exceed 1900° for explosives used for penetrating rock, nor 1500° for work in the coal-seams.

Austria. In Austria shots are fired freely exposed in a mixture of fire-damp and air. The manufacture of explosives is, however, a State monopoly, and for the comparatively unimportant Austrian coal-mines the only explosives permitted are Dynammon and Wetter-dynammon.

Germany. In Germany the law prescribes that only safety explosives may be used in mines in which fire-damp or inflammable coal-dust has been found. The onus of proof as to what constitutes a safety explosive rests with the mine owners, and testing stations have been erected by the Mine Owners Association at Gelsenkirchen and Grube Maria. A number of the explosives factories also possess testing galleries for their own use ; such galleries exist at Haltern, Schlebusch, and Castrop. The gallery at Gelsenkirchen may be taken as typical of a whole class ; it is 34 metres long and elliptical in section with the major axis vertical ; the diameters are respectively 1·80 and 1·35 metres. The charge of explosive is fired without stemming from a cannon with a bore 4 cm. in diameter and 70 cm. deep. This is fixed at one end of the gallery and inclined so that a prolongation of the bore would strike the roof of the gallery about 10 metres from the further end, in order to imitate more closely the condition of an actual shot in a mine. At the end where the gun is, an explosion chamber of 10 cubic metres capacity is formed by means of a paper diaphragm.

Belgium. Although the testing of explosives has only been taken up in Belgium comparatively recently, the work done at the testing station at Frameries by Watteyne and Stassart has advanced the matter considerably. The gallery is similar to the one at Gelsenkirchen, 30 metres long and elliptical in section ; axes 1·40 and 1·85 metres, sectional area 2·0 square metres. The bore of the gun is 5·5 cm. in diameter and 46 cm. long ; it is inclined upwards, and is fired without stemming into an explosion chamber 10 cubic metres in capacity, as at Gelsenkirchen. The explosive atmosphere contains 8 per cent. of purified fire-damp, and is warmed to a temperature of 25°. Tests are also carried out with mixtures of coal-dust and air. A charge is first fired, which is large enough to cause ignition, and then it is gradually diminished, 50 g. at a time, until one is found, which in ten shots causes no ignition. The tests are then repeated in the presence of coal-dust. The maximum charge that can be fired without causing ignition is called the " charge limite." Tests are also carried out in the Trauzl block to ascertain the charge equal in strength to 10 g. of Dynamite No. 1. If the " charge limite " is equivalent to more than 175 g. of dynamite, the explosive is placed on the list of " Explosifs S.G.P." (Sûr-Grisou-Poussières).

England. The testing gallery erected at Woolwich consisted of a comparatively small

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iron tube 27·5 feet (8·4 m.) long and 2·5 feet (0·76 m.) in diameter, circular in section. The bore of the gun was 30 inches (76 cm.) long and $1\frac{7}{8}$ inches (4·8 cm.) in diameter; its axis was parallel with that of the gallery. The strength of the explosive to be tested was first ascertained by firing it into the ballistic pendulum, and then charges of a certain strength were fired stemmed with a fixed amount of dry clay into a mixture of 15 per cent. coal-gas and 85 per cent. air. The details of the test were altered from time to time. The smaller sectional area of the Woolwich gallery rendered the test much more sensitive, and the gas mixture employed was also more easily ignited than those used on the Continent; but, on the other hand, the use of stemming enabled many explosives to pass, which otherwise could not have done so. One of the most remarkable effects of the differences in the tests was that a non-detonating explosive, Bobbinite, was successful in getting placed on the "Permitted List." This has been very popular with miners, as no detonator is required to fire it, and it does not break up the coal so much as a more violent explosive. It caused a number of ignitions without, however, doing any very serious damage, and in consequence of this a Departmental Committee was appointed in 1906 to inquire whether non-detonating explosives should not be excluded entirely from coal-mines. The Committee did not recommend the total exclusion of Bobbinite and similar explosives, but suggested the adoption of a supplementary test on the same lines as that applied at Frameries, and that for operations in mines where there is danger of a widespread explosion of coal-dust, only those explosives should be used which gave a high "charge limite" when fired unstemmed.

A larger testing gallery has now been erected at Rotherham. This is 50 feet (15·2 m.) long and 5 feet (1·52 m.) in diameter; it is circular in section and constructed of iron. The explosion chamber has a capacity of 10 cubic metres. The gun has a bore 2 inches (5·1 cm.) in diameter and 4 feet (122 cm.) long. The cartridges have a diameter of $1\frac{3}{4}$ inches (3·2 cm.). Shots are fired unstemmed into a mixture of air with 13·5 per cent. coal-gas, until the largest charge is found which can be fired without igniting the mixture. Further shots are fired, beginning with this charge and, in the event of an ignition, reducing the charge until five shots of the same weight have been fired without igniting the mixture. Shots are then fired into a mixture of coal-dust and air. The lower of the charges thus determined is known as the "Maximum Charge."

Charges of 4 ounces are also fired at the ballistic pendulum, and the swing obtained is compared with that given by 4 ounces of gelignite containing 60 per cent. of nitro-glycerine.

The Explosives in Coal-Mines Order of March 31, 1913, gave the first list, containing twenty different explosives, which had passed this test, but it was provided that those on the previous list, which had passed the Woolwich test, should still be permitted until December 31, 1913. By the Order of

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September 1, 1913, the use of Bobbinite has been restricted to mines that are not dangerous on account of either gas or coal-dust. With this exception the old list has been abolished. Up to May 13, 1914, forty-six explosives had passed the Rotherham Test.

America. In the United States legislation as regards the use of explosives in coal-

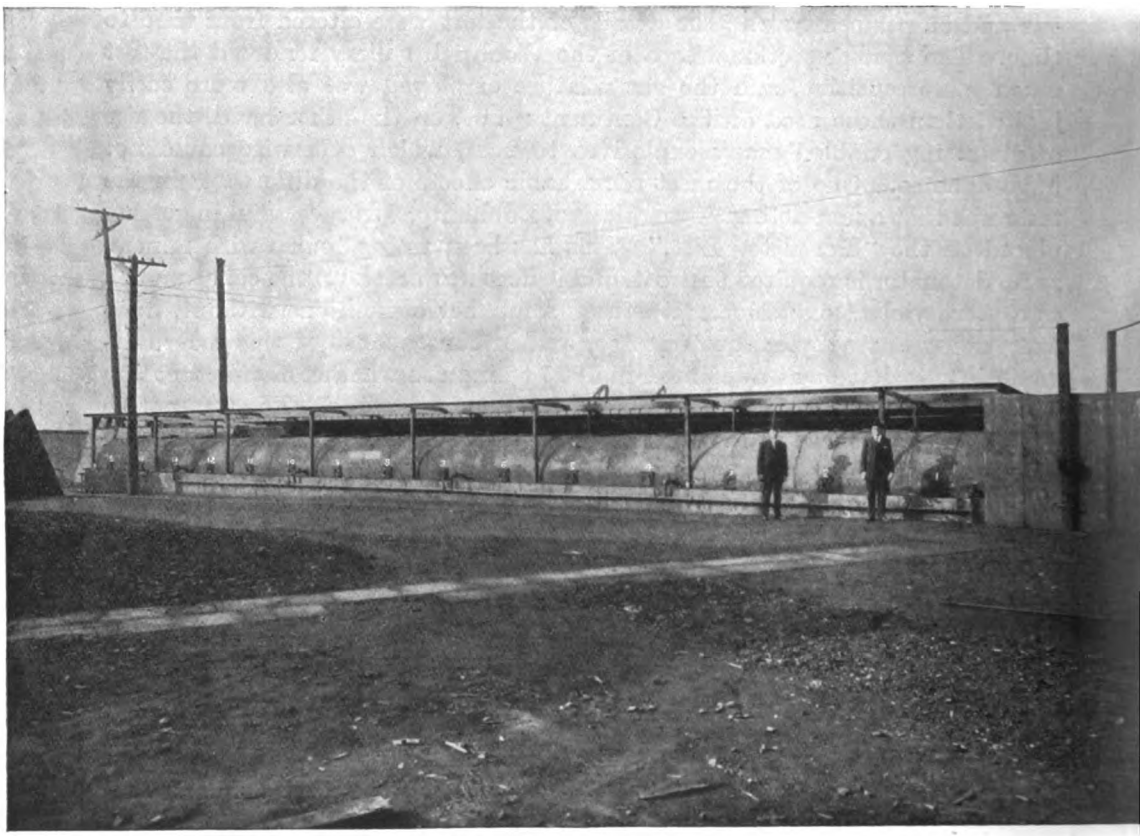

Fig. 112. United States Testing Gallery, Pittsburg, Pennsylvania

mines is in the hands of the individual States. Nevertheless a testing gallery has been erected at Pittsburgh under the charge of the Bureau of Mines of the Central Government (*see* Figs. 112, 113). Here explosives are tested, and as there is no power to order what shall be used, those that are successful in passing the tests are merely placed on a list of "Permissible Explosives." The gallery is circular in section and made of boiler plate; it is somewhat larger than other galleries, having a diameter of 6 feet 4 inches (1·93 m.) and a length of 100 feet (30·5 m.). The bore of the cannon is $2\frac{1}{4}$ inches (5·72 cm.)

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in diameter and 21½ inches (54·6 m.) deep. The explosive gas mixtures are made with natural gas containing about 82 per cent. methane, 16·4 per cent. ethane and 1·5 per cent. nitrogen; tests are also carried out with bituminous coal-dust, ground to pass a 100-mesh sieve. Shots are first fired at the ballistic pendulum to ascertain the charge equivalent to 8 ounces (227 gr.) of standard 40 per cent. American dynamite. Series of ten shots of the equivalent charge are then

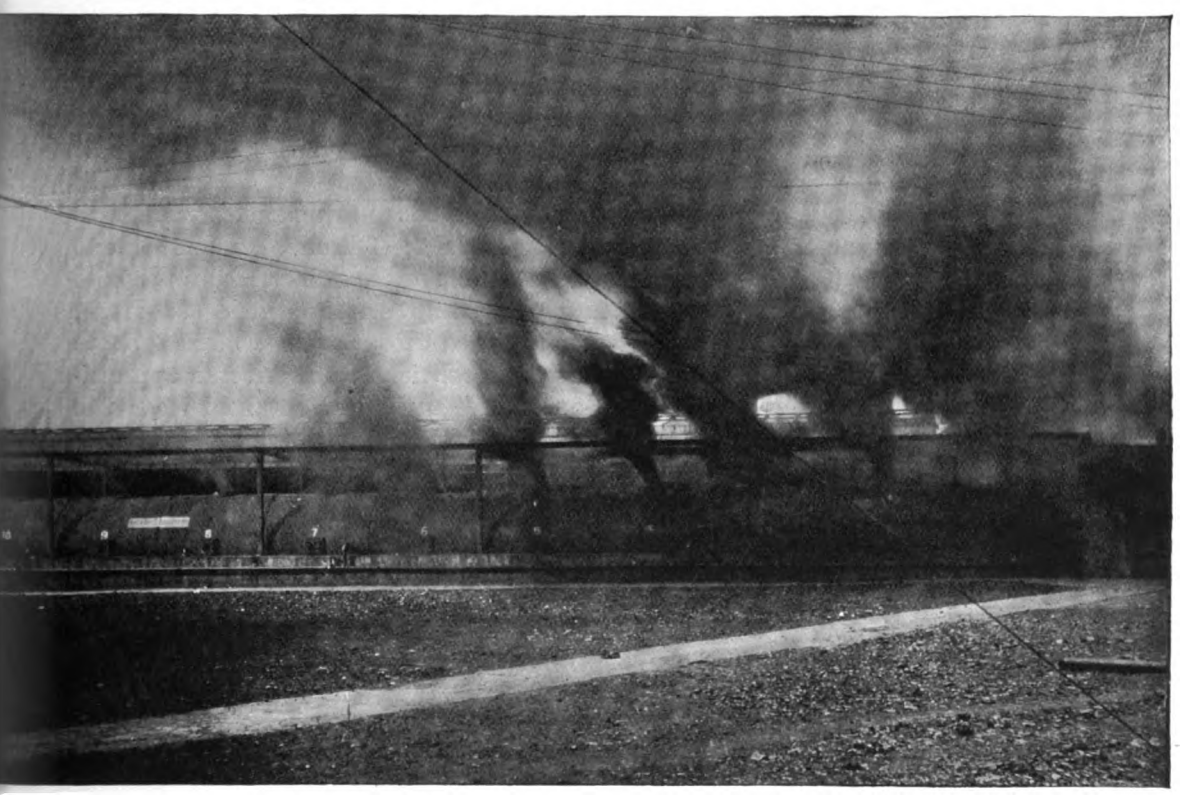

FIG. 113. Explosion of Dust and Gas in United States Testing Gallery

fired into (1) a mixture of gas and air containing 8 per cent. of methane and ethane; (2) a mixture containing 4 per cent. methane and ethane and 20 lb. of coal-dust, and (3) air with 40 lb. of coal-dust only. In each of these tests the equivalent charge is taken and is tamped with 1 lb. of dry clay; the gallery is maintained at a temperature of 77° F. (25° C.). Shots are also fired unstemmed into mixtures of air and 20 lb. coal-dust with 4 and 2 per cent. gas respectively with the object of establishing a limit charge, but as this mixture is somewhat insensitive to ignition by most explosives, all the successful

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explosives failed to ignite with a charge of 1½ lb. (680 g.). Some English explosives, which had passed the Woolwich test, gave only very small limit charges, however. If the equivalent charge be 1 lb. or more, the explosive is not placed on the Permissible List, for such explosives do not break down the coal satisfactorily unless they are used in charges of more than 1½ lb., and such large charges are believed to be dangerous in gassy and dusty mines. A number of other properties of the explosives are observed at the Pittsburgh testing station including: density, Trauzl test, velocity of detonation, height and duration of flame, falling weight test, explosion by influence, pressure developed, heat evolved, and compression of small lead blocks. The results of all these tests on a considerable number of American safety explosives are given in *Bulletins* 15 and 66, but the compositions of the explosives are not stated.

Different systems.

There are three fundamentally different methods of firing explosive charges in testing stations: (1) freely exposed as in Austria; (2) from a cannon without stemming, and (3) from a cannon with stemming. None of these represents at all closely the conditions of a normal blasting shot fired in a coal-seam, but this is not required, because it is recognized that it is the abnormal shots that constitute the greatest danger. The Woolwich test represents approximately the conditions of a "blown-out shot," such as is obtained when the bore-hole is overcharged or insufficiently tamped. Sometimes a bore-hole traverses or passes near to a fissure in the coal containing fire-damp, and it has been found that explosives which have passed the Woolwich test are liable to ignite the gas when this is the case. An unstemmed shot represents this condition of affairs more nearly, and it is principally for this reason that this system of testing is now adopted so generally. The Austrian test imitates what would happen, if a miner accidentally exploded a cartridge which had not been placed in a bore-hole at all, but this is an occurrence which should be very rare, and the general adoption of this test in countries which have extensive coal-mines would hamper the industry too much. The results obtained depend not only on the nature of the explosive that is tested, but also on the dimensions of the gallery and of the cannon, and on the composition, temperature and pressure of the explosive gas mixture used.

Explosive atmospheres.

The explosive atmosphere of the testing gallery is generally made by mixing either coal-gas or fire-damp (pit gas, methane) with air. Fire-damp is the more satisfactory, as it is the gas which actually occurs in the mines, but there are few localities where there is a sufficient and uniform supply of it available; it is liable to be mixed with varying proportions of air and other impurities. It is, therefore, found necessary to purify the gas before use and to analyse the explosive mixture each time. Synthetic methane is unfortunately too expensive to use in the very large quantities

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that are required for these tests. At Rotherham and some other stations coal-gas is used, as it is always available. Its mixtures with air are, however, more liable to explode than those of methane, because in addition to methane it contains considerable proportions of hydrogen and carbon monoxide. In all these gaseous mixtures there is an upper limit of explosibility as well as a lower one, and if the proportion of inflammable gas be raised above it, the mixture will burn but will not explode. These explosive limits have been determined by both Kubierschky [1] and Bunte : [2]

	Explosive limits	
	Kubierschky	Bunte
	Per cent.	Per cent.
Methane	6·0–12·0	6·1–12·8
Hydrogen	9·5–64·7	9·5–66·4
Carbon monoxide . . .	14·3–74·6	16·5–75·0
Coal gas	7·0–22·6	7·9–19·1

There is also a considerable difference in the temperatures at which the different gases are ignited. These temperatures also depend upon the conditions of the experiment. Dixon and Coward [3] found the following :

Methane	650–750°
Hydrogen	580–590°
Carbon monoxide	640–660°
Ethane	560–630°

In the case of methane, ethane and other hydrocarbons, the time during which the gases are exposed to the high temperature and the nature and extent of the heating surface produce much more effect than in the case of hydrogen or carbon monoxide. This is doubtless due to the fact that the hydrocarbons are first converted into aldehydes, which are then further oxidized, as has been shown by Bone and Wheeler. It is not to be expected, therefore, that explosives differing very much as to the temperature and composition of their products will give comparable results when tested in two different testing stations, if in the one case methane is used and in the other coal-gas.

Will [4] carried out experiments in a miniature gallery using different inflammable gases, and found the following limit charges :

[1] *Ang.*, 1901, p. 130.
[2] *J. f. Gasbel.*, 1901, p. 835.
[3] *Trans. C.S.*, 1909, pp. 514–543. *See also* Dixon and others, *I.C.S.*, 1914, pp. 2027, 2037.
[4] *S.S.*, 1909, p. 326.

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	9·8 per cent. Coal-gas	9 per cent. Methane	2·8 per cent. Petroleum ether	24·5 per cent. Coal-gas
	Grammes	Grammes	Grammes	Grammes
Trinitro-toluene	4	8	9	12
Astralite	5	8	8	10
Wetter-Astralite	10	12	12	14
Strengthened Chrom-Ammonite .	10	20	13	13
Ammon-Carbonite . . .	25	25	25	25
Gelatine Wetter-Astralite . .	50	35	30	30
Chrom-Ammonite 1908. . .	65	40	35	35

Although the explosives in every case fall into the same order, the differences with the various gases are considerable. The proportion of methane used at the testing stations is 8 to 9 per cent., which mixture has the greatest degree of sensitiveness. At Rotherham a mixture of 13·5 per cent. coal-gas with 86·5 per cent. air is used, which is the most sensitive mixture of this gas. By using a smaller proportion of gas, a mixture would be obtained with a lower degree of sensitiveness, more nearly approaching that of the methane-air mixtures, but with such mixtures slight variations in the proportions makes a considerable difference in the sensitiveness, and this is not the case with the mixture of maximum sensitiveness.

The fact that at low temperatures there is a considerable retardation in the ignition of methane was pointed out many years ago by Mallard: at 650° he estimated that 10 seconds were required to effect ignition. It is upon this observation that the French official rule which limits the temperature of explosion of explosives was founded, for it was considered that, before the retardation interval expired, the temperature of the products of explosion would be reduced below the ignition point of the explosive atmosphere, provided that the temperature of explosion of the explosive was below 1500°.

Coal-dust.

Tests are now carried out with coal-dust as well as with gas mixtures. The results obtained depend upon the composition and quantity of the dust. In order that the conditions may be as uniform as possible the coal should be freshly ground and sifted. The ease of ignition of the dust depends upon the percentage of matter in it soluble in pyridine,[1] and also upon the degree of fineness to which it has been ground. The coal-dust used at Frameries contains 20 to 22 per cent. of volatile matter, and is ground to pass a sieve with 1280 meshes to the square cm. (91 to the linear inch). Coal with a higher proportion of volatile matter was found not to grind well. The coal-dust used at Rotherham has, according to Lewes,[2] the following composition:

[1] Wheeler, *J.C.S.*, 1913, p. 1715.

[2] *Jour. R. Soc. Arts*, 1913, p. 525.

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Moisture	2·4 per cent.
Volatile matter	29·6 „
Fixed carbon	65·4 „
Ash	3·9 „

and it ignites at 400°. It is ground to pass a 150-mesh sieve. The amount of moisture in the coal-dust also affects the sensitiveness of the test.

Influence of size of bore.

The influence of the size of the bore of the cannon has been investigated by Hatzfeld at Neunkirchen.[1] Two different cannon were used: the first had a bore of diameter 5·5 cm. and a depth of 57·5 cm., and the other a diameter of 4 cm. and a depth of 70 cm. Tests were carried out with the following three explosives:

(1) Carbonit I		(2) Chrom-ammonite		(3) Wetter-sicheres Gelatine-Dynamit III	
Nitro-glycerine	25	Ammonium nitrate	66	Nitro-glycerine	28·0
Sodium nitrate	30½	Potassium nitrate	14½	Collodion cotton	0·7
Potassium bichromate	5	Chrome ammonia alum	10	Dinitro-toluene	11·0
Wheat flour	39½	Collodion cotton	9	Ammonium nitrate	37·0
		Vaseline	½	Rye flour	4·0
				Sodium chloride	19·3

Of these, chrom-ammonite is now no longer made. Shots were fired into mixtures of fire-damp and air containing 8 to 9 per cent. methane, and also into air mixed with various quantities of coal-dust, of which 2 litres were suspended in the air, whilst the remainder was spread about in the explosion chamber. The charges were fired electrically with a No. 8 detonator. The following Table gives the limit charges:

Diameter of bore-hole	Diameter of cartridges	Explosive mixture	Limit charges of explosive		
			(1)	(2)	(3)
In open	35 mm.	Fire-damp	150	200	50
55 mm.	35 „	„	>700	>700	50
55 „	55 „	„	200	550	50
55 „	35 „	12 litres dust	>700	>600	>700
55 „	55 „	„	450	>700	>700

[1] *S.S.*, 1910, p. 221.

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Diameter of bore-hole	Diameter of cartridges	Explosive mixture	Limit charges of explosive		
			(1)	(2)	(3)
55 mm.	35 mm.	7 litres dust	>700	>600	>700
55 ,,	55 ,,	,,	>700	>700	>700
40 ,,	35 ,,	Fire-damp	>700	>650	250
40 ,,	40 ,,	,,	600	>600	300
40 ,,	35 ,,	12 litres dust	>700	>700	>700
40 ,,	40 ,,	,,	>600	>600	>700
40 ,,	35 ,,	7 litres dust	>700	>700	>700
40 ,,	40 ,,	,,	>600	550	>700
40 ,,	35 ,,	2 litres dust	>700	650	>700
40 ,,	40 ,,	,,	>600	500	>700

In practically all cases the explosives were more dangerous when they were concentrated at, and completely filled, the bottom of the bore. Under these conditions the charge would explode in a smaller interval of time, and would consequently give a more violent blow, and the gas mixture at the mouth of the cannon would be heated more strongly adiabatically. In their behaviour towards the various explosive atmospheres the three explosives show characteristic differences. Carbonite on explosion gives a large proportion of reducing gases ; when fired from a hole of large diameter at a high density, the explosive is not very safe towards either fire-damp or coal-dust, and this is ascribed to ignition of the combustible products when they have been ejected and mixed with the air. When loaded at lower densities, or fired in a smaller bore, the gases are cooled so much before they reach the mouth that they no longer ignite in the air. Chrom-ammonite, like most ammonium nitrate explosives, contained an excess of oxygen. Consequently there was no danger of the formation of a secondary flame as in the case of carbonite. The explosive showed a high degree of safety under all conditions. The products of explosion of the gelatine dynamite occupy an intermediate position, as the explosive contains nearly enough oxygen for complete oxidation, but not quite. With fire-damp it is the worst explosive of the three, but in the presence of coal-dust it is safe. All three explosives show a lower degree of safety in the larger bore, but this is specially marked in the case of the third. It is true that such large holes are not usually drilled in coal-mines, but when a shot blows out without doing its proper work, it enlarges the bore somewhat ; it is, therefore, desirable to test the explosives in a large hole.

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Dimensions of gallery.

It has long been recognized that in a gallery of small sectional area there is greater tendency to cause ignition than in a large one. This question has been investigated at Frameries by Watteyne and Bolle.[1] The explosion chamber of the testing gallery was altered by inserting iron tubes of different diameters, extending from the end, where the cannon is, up to the diaphragm. In this way galleries were obtained with sectional areas of 0·28 and 0·95 square metres, in addition to the ordinary gallery having a sectional area of 2 square metres. Representative explosives of the different types, which have been successful in passing the Frameries tests, were all tried. The following Table summarizes the results obtained: for each explosive the "charge limite" obtained with fire-damp in the 2 square metres gallery is taken as unity, and the "charges limites" under the other conditions are expressed as fractions of this.

Type	Explosive	Tests in fire-damp			Tests in coal-dust		
		0·28 sq. m.	0·95 sq. m.	2 sq. m.	0·28 sq. m.	0·95 sq. m.	2 sq. m.
Safety dynamite .	Dynamite antigrisouteuse V	0·46	0·46	1	≥ 1	≥ 1	≥ 1
Carbonite . .	Kohlen-carbonite.	0·72	0·94	1	0·06	0·28	≥ 1
Gelatine dynamite	Colinite antigrisouteuse B.	0·56	0·81	1	0·50	≥ 1	≥ 1
Ammonium nitrate	Fractorite D. .	0·36	0·79	1	0·21	0·43	≥ 1
,, ,,	Favier 3bis .	0·33	0·80	1	0·87	≥ 1	≥ 1
Perchlorate . .	Permonite . .	0·06	0·67	1	0·61	≥ 1	≥ 1

The reduction of the "charge limite" with diminution in the diameter of the gallery is only slight with the carbonite when fired into fire-damp, but when coal-dust is present the reduction is very great. The gelatine dynamite contains an equally high percentage of nitro-glycerine, and its products are as combustible as those of the carbonite, but instead of potassium nitrate it contains ammonium nitrate and potassium perchlorate, and this evidently increases the safety. The ammonium nitrate explosives show considerable reduction, as also does Permonite in fire-damp, but not in dust.

It has been proposed by Will [2] to test explosives in a small gallery 3 metres long and 0·21 square metres in section. This might be convenient to manufacturers for making preliminary tests of explosives, but the above figures show that the results could only be received with great caution.

[1] *Annales des Mines de Belgique*, vol. xvi., pp. 289–320; *S.S.*, 1911, pp. 321, 344, and 371.
[2] *S.S.*, 1909, p. 323.

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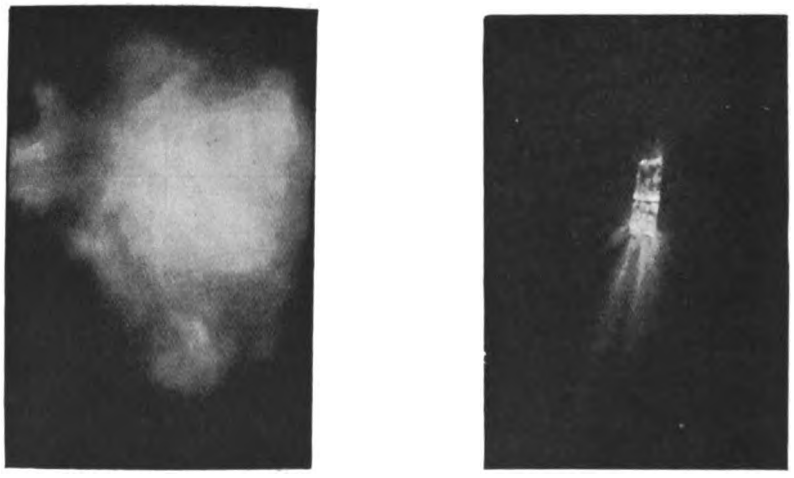
At Liévin numerous experiments have been carried out to ascertain the effect of various factors on the safety of explosives. Various conclusions have been arrived at, which although they leave much yet to be discovered, assist considerably in the comprehension of the matter. These researches were reported on by Taffanel and Dautriche at the 8th Inter. Cong. Appl. Chem., 1912.[1] Complete decomposition, according to the theoretical formula, is nearly always attained in a closed bomb, provided that the density of loading be not too small; and it seems also to be attained in practice in bore-holes that are well tamped; but with most explosives decomposition is very in-

Incomplete decomposition.



Blasting Gelatine — Wetter-Dynamon

FIG. 114. Detonated in the Open. Photographs by Wilkoszewski

complete when they are fired in the steel cannon at the testing stations; when fired in the open air decomposition is still more incomplete. The heat generated was estimated from the pressures registered when the explosion was effected within a very capacious vessel. With safety explosives (Grisoutine, Grisounite, Kohlencarbonite, Sabulite) only about 70 per cent. of the theoretical quantity of heat was evolved when they were fired in a cannon, and only 40 per cent. when unconfined. Dynamite No. 1, on the other hand, detonates almost completely even when unconfined, and so does blasting gelatine, provided that a very powerful detonator be used. These results were confirmed by analyses of the gases: the free oxygen evolved by the safety explosives was considerably less than the theoretical, there were traces of carbon monoxide and sometimes of hydrogen, and considerable quantities of oxides of nitrogen.

[1] Vol. iv., p. 127.

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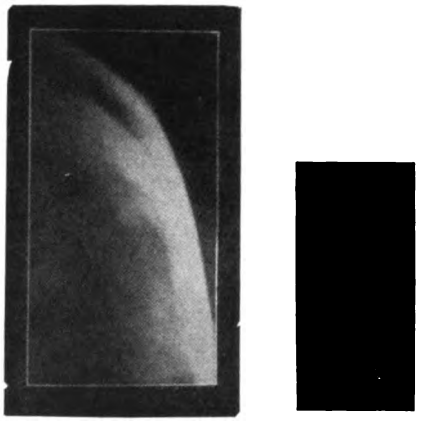
Flames.

The liability of an explosive to ignite fire-damp or coal-dust depends, of course, very largely upon the nature of the flame, which it gives when exploded. These flames have been studied by means of photographs for many years past.[1] Bichel, realizing that the time of duration of the flame is of as great importance as its length, photographs through a vertical slit the image of the flame on a sensitive film fixed to a drum which rotates about its vertical axis.[2] He thus obtains an inclined image the height of which gives the length of the flame and the width the duration (*see* Fig. 115). The explosive is fired in a cannon similar to those used at the testing galleries.



20 g. Blasting Gelatine — 100 g. Ammon-Carbonite

FIG. 115. Flame Photographs by Bichel

The following Table gives some of the results of Bichel's flame measurements :

100 grammes of	Duration secs.	Length mm.	After-flame Ratio
Gunpowder	·077	110	1 : 330
Blasting gelatine	·0097	224	1 : 883
Guhr dynamite	·0083	228	1 : 620
Gelignite	·0012	150	1 : 101
Trinitro-toluene	·0016	108	1 : 1347
Picric acid	·0015	110	1 : 1050
Gun-cotton	·0013	97	1 : 81
Donarite	·00040	69	1 : 15
Ammon-Carbonite	·00028	51	1 : 7·4
Carbonite	·00033	40	1 : 6·5
Kohlen-carbonite	·00031	41	1 : 8·7

The flames from the safety explosives have less duration and length than the others. Other things being equal an explosive with a high velocity of detonation may be expected to give a flame of less duration than a slow one. But a very high velocity of detonation is undesirable in a safety explosive, because it is liable to ignite the explosive gas mixture by the rise of temperature caused

[1] *See* Guttmann, *J.S.C.I.*, 1899, p. 7 ; Wilkoszewski, *S.S.*, 1907, p. 141.
[2] *Testing Explosives*, 1905, p. 43 ; *S.S.*, 1908, p. 408.

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by the sudden compression. Bichel, therefore, divides the time of detonation of the charge by the duration of the flame and the figures thus obtained, which

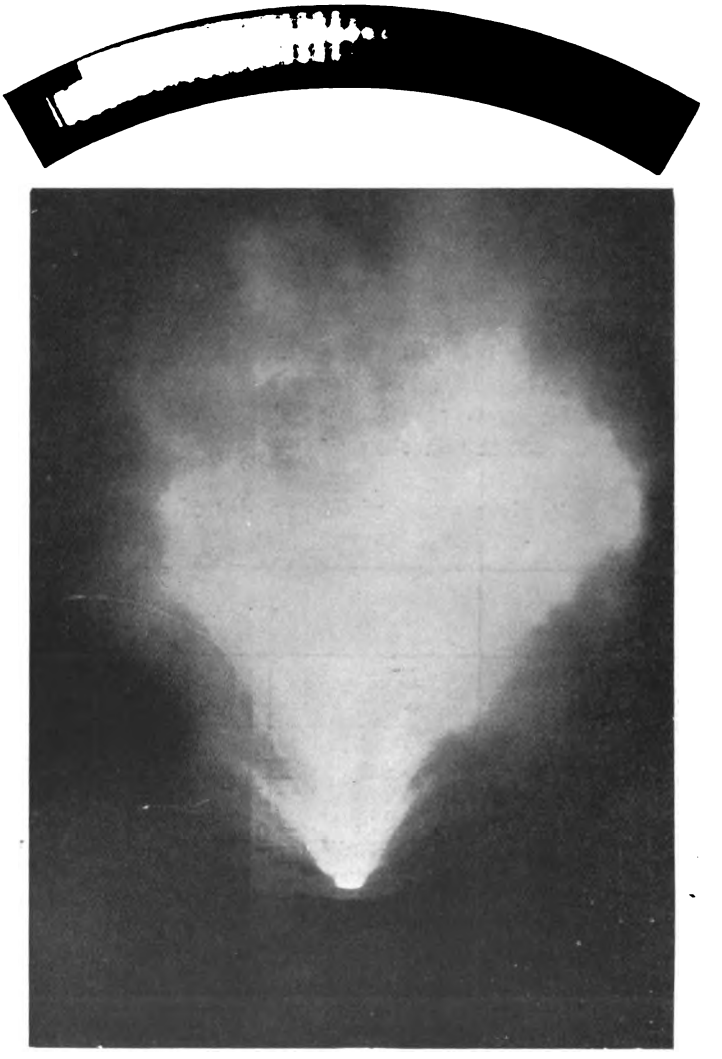

FIG. 116. Flame from Kieselguhr Dynamite

he calls the "after-flame ratio," he finds of use in judging the safety of the explosive.

Will photographs the flames in a somewhat different manner:[1] over a

[1] *S.S.*, 1909, pp. 323, 343.

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circular strip of sensitive film he places a metal disc with numerous small slits in it, and the film and disc are rotated together rapidly behind a small opening, in front of which the cannon is fired. At the same time a photograph of the flame is taken with an ordinary camera (*see* Figs. 116 to 120). These photo-

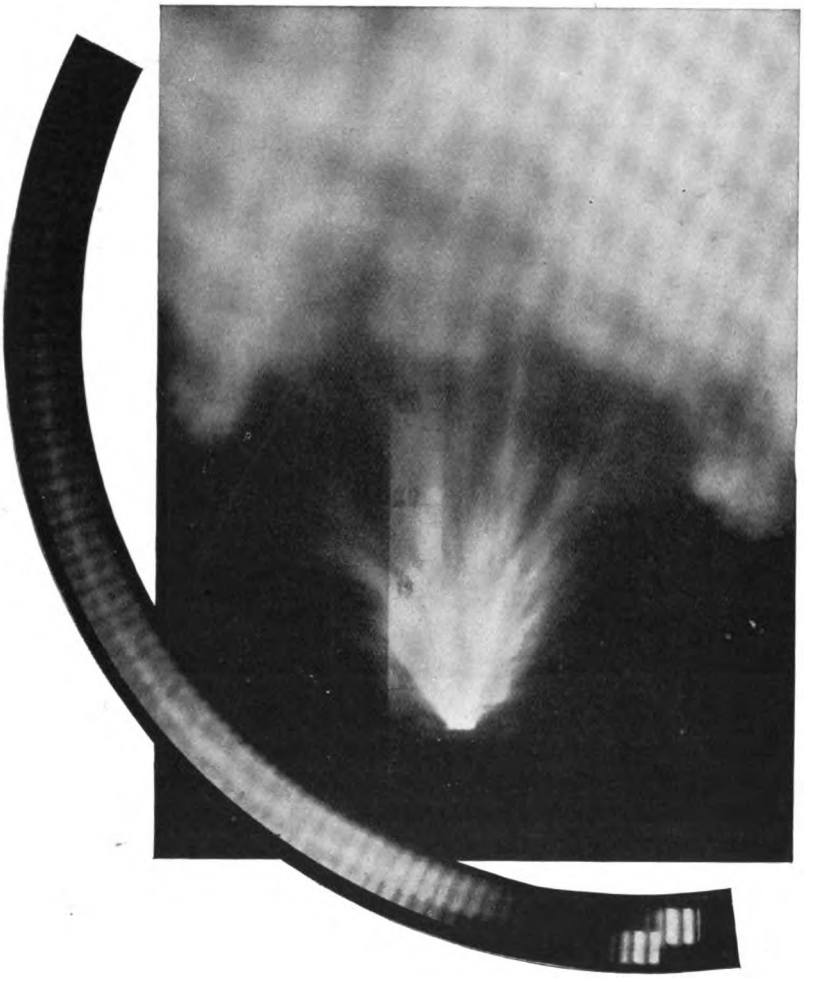

FIG. 117. Flame from Gun-cotton

graphs bring out very clearly the secondary flames formed when the products from explosives poor in oxygen, such as gun-cotton, trinitro-toluene or picric acid, become mixed with the air in front of the mouth of the cannon. These secondary flames can be prevented largely or entirely by mixing a few per cent. of an alkali salt with the explosive.

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Effect of alkali salts.

This effect has been confirmed by Dautriche [1] by estimations of the total heat produced when the explosives are fired inside a closed vessel having a capacity of 10 cubic metres, the number of calories being deduced from the pressure generated.

	Heat generated by 100 g.	Heat calculated	
		(*a*)	(*b*)
	cals.	cals.	cals.
Gun-cotton alone	184	96	242
with 0·5 per cent. $NaHCO_3$ . .	146		
1 per cent. ,, . .	88		
2 per cent. ,, . .	89		
2 per cent. KNO_3 . . .	88		
3 per cent. K_2SO_4 . . .	79		
2 per cent. $CaCO_3$ . . .	152		
4 per cent. $MgCO_3$ . .	152		
10 per cent. ,, . . .	140		
3 per cent. $Pb(NO_3)_2$ . .	140		
Trinitro-toluene alone	>250	66	354
with 2 per cent. KNO_3 . . .	117		
3 per cent. ,, . . .	96		
4 per cent. ,, . . .	82		
5 per cent. ,, . . .	66		
10 per cent. ,, . . .	66		
6 per cent. $Ba(NO_3)_2$ . .	187		
10 per cent. ,, . .	175		

The figures in column (*a*) are calculated for simple detonation, those in (*b*) for complete oxidation of the products of detonation by the oxygen in the air within the vessel. It will be seen that the salts of the alkalies are much more effective, in preventing the secondary oxidation, than those of the alkaline earths or lead. This is probably due to dissociation of the alkali compounds at the high temperature of the flame, the temperature being thus reduced below the ignition point; the elements recombine at a fairly high temperature so that the heat is available for doing work in blasting.

Also with explosives containing an excess of oxygen the safety is increased by the substitution of a few per cent. of saltpetre for the same amount of ammonium nitrate; the oxidation of the methane by the heated oxygen is, no doubt, similarly prevented by the reduction in the temperature.

[1] *P. et S.*, vol. xv., 1910, p. 164.

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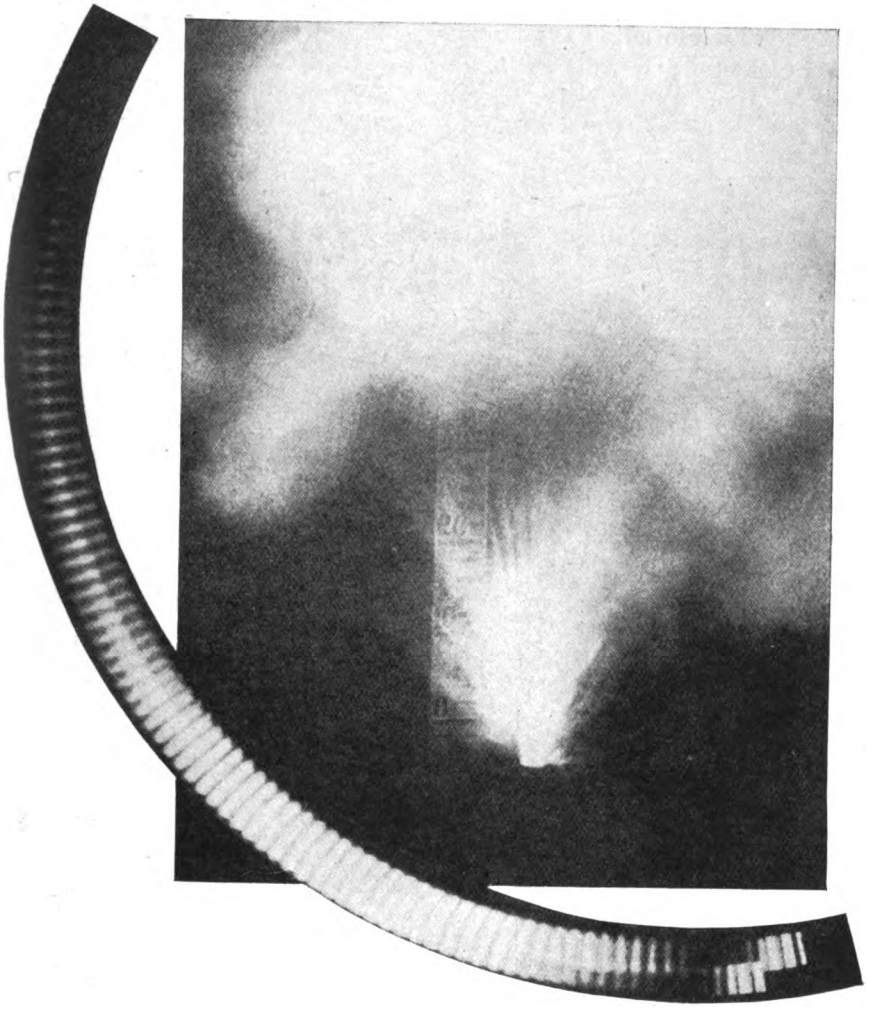

FIG. 118. Flame from Picric Acid

	Charge limite, in grammes	
	Without saltpetre	With saltpetre
Grisounite couche	660	>840
Grisounite roche	240	>670
Grisoutine roche	100	220

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With coal-dust the alkaline salts have no marked influence, which shows that the mechanism of the ignition is different.

Effect of density.

The density to which an explosive is compressed has a great influence on the velocity of detonation, and the consequent effect upon the safety of the

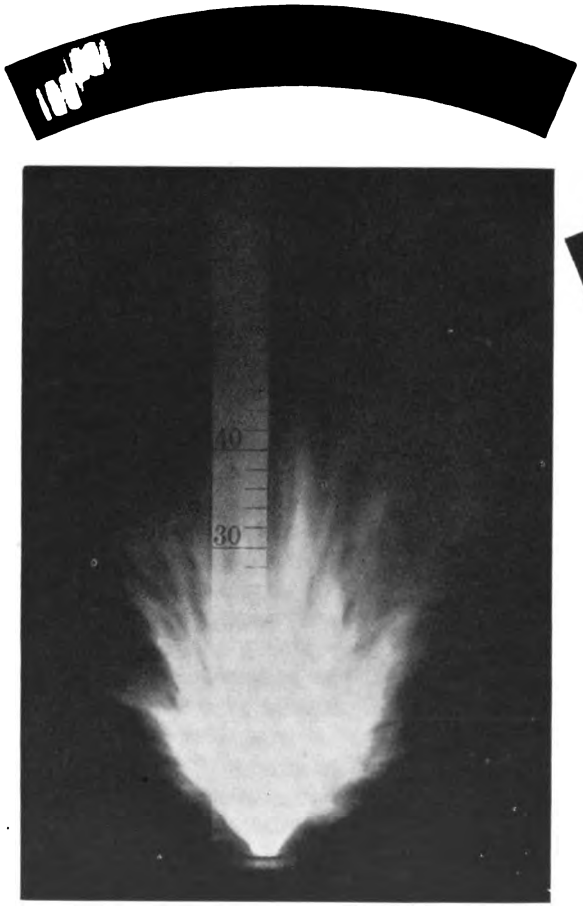

FIG. 119. Flame from Picric Acid with 5 per cent. Sodium Bicarbonate

FIG. 120. Flame from Ammoncarbonite

explosive is in some cases even more marked. Thus Taffanel and Dautriche [1] give the following figures for Grisoutine roche :

Density	Charge Limite
1·4–1·5	150 g.
1·3–1·4	725 g.

[1] *Eighth Int. Cong. App. Chem.*, 1912, vol. iv., p. 136.

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There was no great difference in the amount of heat evolved, and the "charge limite" of the dense explosive was only raised to 200 g. when it was made up into smaller cartridges. The effect is, therefore, evidently due to the variation in the velocity of detonation. For every explosive there is a critical density, which cannot be exceeded without reducing the "charge limite." This critical density varies according to the nature of the explosive and the amount of moisture in it; sometimes, but not always, it coincides with the limiting density from the point of view of the velocities of detonation. As it is not far removed from the densities to which the cartridges are usually compressed, slight variations in the manufacture of the cartridges, or in the percentage of moisture, may affect greatly the maximum charge that can be fired without causing ignition.

Incorporation.

If the ingredients of a safety explosive be not thoroughly incorporated together, the explosion may be greatly affected, and in different cases opposite effects may be produced. Thus in the case of "Grisounite couche" fired in the open, bad incorporation improved the "charge limite," whereas with a Kohlen-carbonite fired in a cannon in the presence of coal-dust, the "charge limite" was reduced. The granulation of the explosive also has an influence.

Wrappers.

The nature of the material surrounding the cartridge has considerable influence. Taffanel and Dautriche give the results of analyses of gases evolved when "Grisounite roche" is fired from the cannon under various conditions; the means of their results are:

	Oxygen	Combustible gases
	per cent.	per cent.
Theoretical decomposition	11·4	0
No wrapper	− 1·1	2·4
No wrapper, a little stemming	1·5	4·0
Asbestos paper wrapper	2·0	1·6
Paraffined paper wrapper	− 1·8	20·0
„ „ „ a little stemming . .	− 1·5	13·0
Aluminium foil wrapper	− 1·8	2·0
Tinfoil wrapper	− 1·4	2·0
Paraffined paper and 20 g. powdered coal . .	0	37·5
Tinfoil and 20 g. powdered coal	− 1·1	55·6

The combustible gases comprised carbon monoxide, hydrogen and methane. Considerable quantities of oxides of nitrogen were also formed, including about 3 per cent. of the suboxide N_2O, and some NO which combined with the oxygen of the collecting vessel and caused the deficits of oxygen which were recorded. The figures show that even an explosive containing a large excess of oxygen

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may give a large proportion of combustible gas. Large secondary flames were obtained in some cases and were recorded photographically. When formed, they greatly reduce the " charge limite," as is shown in the following Table. The " charge limite " in the presence of coal-dust is increased when the amount of paraffin and coal round the cartridge exceeds a certain amount, probably because the temperature of the products is reduced below the ignition point ; but it is better to secure this by more certain means, such as the addition of alkali salts.

Nature of wrapper	Explosifs couche				Explosifs roche			
	Grisou-naphthalite		Grisou-dynamite		Grisou-naphthalite		Grisou-dynamite	
	Ordinary	With saltpetre	Ordinary	With saltpetre	Ordinary	With saltpetre	Ordinary	With saltpetre
TESTS WITH FIRE-DAMP								
Ordinary paper	750	1050	1075	—	—	—	< 50	—
Paper slightly paraffined	500	675	—	—	<100	375	—	—
Paper strongly paraffined	175	> 600	150	>400	75	200	< 50	300
TESTS WITH DUST								
No wrapper	—	—	—	—	550	—	650	—
Ordinary paper	>1000	>1000	> 810	—	500	>960	550	>600
Paper slightly paraffined	375	260	—	—	—	—	—	—
Paper strongly paraffined	225	200	360	< 50	< 90	75	< 50	> 50
Asbestos paper	>1400	—	>1290	—	700	—	525	—
Brass	675	—	—	—	—	—	—	—
Iron	550	490	1075	—	220	—	400	—
Tin	> 700	—	> 780	—	430	—	310	—
Aluminium	240	—	—	—	—	—	—	—
Asbestos paper surrounded by coal	175	—	—	—	—	—	—	—
Ordinary paper surrounded by coal	90	180	275	—	—	>800	175	175
Paper slightly paraffined and coal	125	125	—	—	—	—	—	—
Paper very strongly paraffined and coal	> 425	> 900	—	—	—	—	—	—

The above results were obtained by firing cartridges 40 mm. in diameter from a cannon 55 mm. in diameter with no stemming.

Length of the cannon.

The " charge limite " depends not only on the diameter of the bore of the cannon but also on its length. The following results were obtained with a

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bore 55 mm. in diameter, which was shortened progressively by plugging the bottom with clay. The explosive used was " Grisou-dynamite roche " containing saltpetre :

Length of bore	1·20	1·15	1·00	0·60 metre
Charge limite	275	375	450	525 grammes

This great increase in the " charge limite " cannot be ascribed to the alteration in the position of the charge with respect to the orifice, for if it be left at 0·60 m. from the mouth, with all the clay removed from the cannon, the " charge limite " is again 275 g. Apparently it is the great surface of metal exposed to the products of explosion, which causes the reduction ; and, in fact, it was found by experiment that there was an increase in the amount of heat.

Stemming. The use of stemming greatly increases the " charge limite." The stemming should be in contact with the charge. The safety can be further increased by placing a quantity of incombustible powder before the mouth of the bore-hole.[1]

Failure to detonate. It is important that cartridges of explosive should not be broken by careless loading of the bore-hole. For if the explosive become mixed with coal-dust, it may fail to detonate and merely burn, when the detonator is fired. The flame from a charge that is consumed in this way can hardly fail to cause the ignition of fire-damp, if it be present, or of coal-dust, if there be sufficient in the air in the vicinity of the bore-hole.[2] Pulverulent explosives containing excess of oxygen are especially liable to behave in this way. The use of a powerful detonator reduces the danger.

Conclusions. The manufacturers of explosives have shown great skill in devising mixtures, which shall pass the tests applied in the different testing galleries, and of late years much has been done to investigate the various conditions which cause or prevent ignitions in these galleries, but unfortunately the conditions, under which the charges are fired, are very different from those that prevail in coal-mines. The next step should be to endeavour to devise tests that shall more accurately select explosives that give a reasonable degree of safety. The greatest difference between the conditions in the mine and in the testing gallery is that in the latter the shot is fired in a steel cannon, and in the former in coal, which may be fissured. Another important difference lies in the fact that in the testing gallery the tests are carried out at ordinary atmospheric pressure, but some coal-mines are several thousand feet deep, and consequently the pressure is considerably greater. This high pressure increases the danger of explosion, but it is improbable that the small variations of atmospheric pressure at the surface can have any marked effect on the explosibility of mixtures of air with gas or coal-dust. It has been suggested that when the barometer

[1] *See* Watteyne and Lemaire, *S.S.*, 1912, pp. 21, 43 and 72.
[2] *See* Dautriche, *P. et S.*, vol. xiv., p. 5.

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is falling there is a greater tendency for the fire-damp to escape from the coal. On the other hand, attempts have been made to prove that the majority of mine explosions occur when the barometer is rising.

The strict supervision over the use of explosives in mines has undoubtedly diminished very greatly the loss of life, but the improvements in ventilation and other precautions are also responsible very largely for this diminution.

Classification. The various classes of safety explosives have been dealt with in previous chapters. They may be divided into the following classes :

Black powder mixtures (Bobbinite).

Gelignites with cooling agent.

Carbonites.

Ammonium nitrate explosives containing a little nitro-glycerine.

Ammonium nitrate explosives containing nitro-aromatic compounds but no nitro-glycerine.

Chlorate and perchlorate explosives.

There are a few, such as Colinite antigrisouteuse B, which do not fall strictly into any of these categories, or might be placed in several of them.

The temperature of explosion may be reduced by having a considerable excess of oxygen or of oxidizable matter, but in either case the explosive becomes rather dangerous in the mine under certain conditions. The presence of salts of the alkalies increases the safety, and the temperature of explosion can also be reduced by the addition of inactive cooling agents such as magnesium sulphate or ammonium oxalate. These introduce no fresh sources of danger, but they diminish the power of the explosive.

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CHAPTER XXXII

FIREWORKS

Rocket : War rocket : Life-saving rocket : Display rocket : Sound rocket : Light rocket : Coloured lights : Golden rain : Phosphorus-chlorate mixtures

FIREWORKS are filled with mixtures, which burn energetically and contain in themselves the oxygen necessary for combustion. These mixtures are practically identical with some of those that are used as explosives, and in some circumstances they are liable to explode. Many varieties of fireworks are made to explode in order to produce a report. One of the materials that is very largely used in pyrotechny is mealed powder, to which substances are added to modify its properties or make it burn more slowly.

Rocket.

FIG. 121. Rocket

The rocket consists of a tube, open at one end, into which is rammed black powder mixture. A long conical hole is then bored into the composition (*see* Fig. 121), and a piece of quick-match or other igniting device is applied. The composition burns from the surface of the conical hole outwards, and the products of combustion, largely gaseous, escape at a high velocity through the constricted opening, with the result that the rocket is driven forwards. For convenience of loading the composition is sometimes compressed into pellets before being placed in the rocket case. The mixtures used vary considerably in composition :

Saltpetre	57–89 per cent.
Charcoal	16–33 „
Sulphur	9–16 „

The compositions that burn most quickly are those that do not differ very much from ordinary gunpowder. The incorporation is generally carried out in drums ; it is not necessary to mix the ingredients very intimately. The charcoal is often not powdered very finely, in order that a good trail of sparks may be formed as the rocket rises.

The ordinary rocket is attached to a stick which projects behind, and

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serves to maintain the direction as it travels through the air. It is from this that the appliance derives its name, for in Old English and other European languages a distaff was called a "rock." Incendiary rockets were used in warfare as early as the thirteenth century apparently,[1] but appear to have done serious damage only rarely, until they were greatly enlarged and improved about the year 1800, when Colonel Congreve devised his war rocket. This consisted of a strong steel tube which had a cast-iron head and a tailpiece with three conical openings or vents cut away on one side, so that the gas issuing from the body met with resistance on one side only, and so caused the rocket to rotate. The rotation kept the rocket steady during flight and consequently no stick was required. The large war rocket weighed 24 lb. and was about 2 feet long. It was used with great effect during the Napoleonic wars, against Copenhagen, at Walcheren and at the battle of Leipzig, but in consequence of the great improvements in artillery it is never used now. The future may see it revived, like the grenade. A powerful rocket with a charge of high explosive in the head and an impact fuse might prove very effective against an enemy shielded from direct fire, and would be comparatively easy to transport in difficult mountain country. Its worst defect is want of accuracy. Major Unge has attempted to revive it under the name of "aerial torpedo" for the attack of air-ships, but for this purpose it does not seem to be suitable.

War rocket.

Life-saving rocket. The life-saving rocket is used by coastguards and others for throwing life-lines on to wrecked ships. It is a powerful rocket so constructed as to burn for a long time and to put only a moderate strain upon the line.

Display rocket. The rocket used for pyrotechnic displays has a cardboard case and a chamber in the forward end, separated by a plug of clay or other material through which passes a piece of quick-match. The chamber contains gunpowder and a number of stars, composed of white or coloured light composition and primed with mealed powder. When the rocket has reached its maximum height and all the rocket composition has burnt away, ignition is conveyed by the quick-match to the powder, which explodes and bursts the walls of the chamber. The stars then fall down burning brightly. The signal rockets used for military purposes are constructed in the same way.

Sound rocket. Sound rockets, which are also used for signals, have a small charge of tonite or other high explosive, which is fired by means of a detonator as soon as the rocket composition has burnt away.

Light rocket. Light rockets are used to light up the landscape and reveal the position of the enemy at night. Each rocket usually contains a single star composed of magnesium light composition somewhat similar to that used for photography. This consists of powdered magnesium or magnesium-aluminium alloy mixed with oxidizing materials such as barium nitrate and potassium chlorate.

[1] *See* Hime, *Gunpowder and Ammunition*, p. 172.

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Coloured lights are used not only for the stars of rockets but also for Bengal lights and very many other sorts of fireworks. In books devoted to pyrotechny many different formulæ may be found, but it may be stated generally that for **Coloured lights.**

green lights	barium compounds
yellow lights	sodium compounds
blue lights	copper compounds
red lights	strontium compounds

are used. Fire-workers like to use the chlorates of these elements together with sulphur or a sulphide, as such mixtures are very easily ignited and burn with great brilliancy. But such compositions are decidedly dangerous: not only are they very sensitive to blows and friction, but they are even liable to ignite spontaneously. The sulphur is oxidized by the chlorate to sulphuric acid, which then accelerates the reaction until it becomes so rapid that the mass ignites. Mixtures containing sulphur are considerably worse than those with sulphides, and after a number of fatal accidents had occurred the use of the sulphur-chlorate mixtures was definitely forbidden by Order in Council No. 15 of April 30, 1894. A similar order has also been issued recently in India, partly because these mixtures were used by Indian anarchists, but in consequence of the difficulty of enforcing such a regulation in a country like India, they are still made by village firework makers, and lead to many fatal accidents. In the year 1910–1911, reports were received of sixteen accidents with these mixtures, causing death to twenty-three persons and injuries to fifty-three, and probably there were many other cases which were not reported. In 1912–1913 there were eight accidents, which killed two persons and injured eleven.

Mixtures of chlorates with the sulphides of arsenic, antimony and copper are also dangerous.[1] Shellac, which is much used for binding the composition together, increases the sensitiveness.[2] Mixtures of chlorate, metallic aluminium and shellac are specially dangerous and may ignite spontaneously if kept at a temperature of 100° F. (38° C.). In many cases the chlorates may be replaced with advantage by the more stable perchlorates. In most countries mixtures of chlorate and sulphur are still allowed. Even in England it is permitted to prime chlorate stars with mealed powder, which is usually applied moist, and a small quantity of chlorate-sulphur mixture is thus formed; several accidents have been ascribed to this cause. Sodium chlorate compositions are more dangerous than those containing the potassium salt.

The following are some examples of coloured fire mixtures:

[1] *See A.R.*, 1905, p. 219; *S.R.*, No. 195, p. 6.
[2] *See S.R.*, No. 148.

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Green		Yellow		Red	
Barium chlorate	66	Sodium nitrate	70	Potassium chlorate	78
Milk sugar	33	Sulphur	20	Strontium carbonate	15
Shellac	1	Antimony sulphide	7	Shellac	7
		Lampblack	3		

Blue		White	
Potassium chlorate	45	Saltpetre	66
Shellac	5	Sulphur	16
Charcoal	5	Antimony sulphide	16
Basic copper carbonate	10	Gelatine	2
Calomel	35		

The compositions have to be varied somewhat according to the rapidity with which they are required to burn, and the conditions of use. For blue light, alum is sometimes used instead of, or in addition to, copper compounds. To white lights lead oxide or nitrate is added in some cases to intensify the effects. Calomel (mercurous chloride) is often added, especially to blue and red lights, to increase the luminosity and decrease the rate of burning.

Golden rain.

Golden rain is made by mixing powder, such as is used for rockets, with crushed iron or steel turnings or borings. These materials are also often added to the rocket mixtures in order to produce a more brilliant trail. If the borings are uncrushed, comparatively few sparks are formed, but they are finer individually and give a good scintillating effect. Magnesium powder gives white sparks; copper, greenish ones; and zinc, bluish white.

Phosphorus-chlorate mixtures.

Mixtures of chlorates with phosphorus are considerably more dangerous than those with sulphur, and their use in fireworks was restricted by Order in Council No. 19 of January 12, 1905, which directs that "no firework which contains an admixture of phosphorus (whether or not in the amorphous form) with chlorate of potassium or other chlorate, shall be manufactured, imported, kept, conveyed, or sold, unless such firework shall have been specially licensed by the Secretary of State for manufacture or importation, and unless it is named and defined in a List of Authorized Explosives signed by a Government Inspector and in force for the time being." Restrictions are imposed in order to ensure that the articles manufactured shall not be capable of exploding in bulk. Thus an Alarm Cork is not allowed to contain more than 0·4 grain (0·026 g.) of mixture, of which not more than 15 per cent. may be phosphorus (amorphous). Amorces or caps for toy pistols and similar articles must not contain more than 70 grains of composition per 1000, of which not more than 10 grains may be phosphorus. Fulminate of silver is also used, but in this case the quantity must not exceed 15 grains (1 g.) per 1000. In Germany only 0·5 g. per 1000 is permitted; on the other hand the charges of chlorate and phosphorus in explosive corks are comparatively large, and a number of fatal accidents have occurred through their exploding in bulk both in Germany and in the United States, whither they were allowed to be exported until a few years ago.

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PART X

STABILITY, ETC.

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CHAPTER XXXIII

BUILDINGS, ETC.

Construction : English distances : German distances : Austrian : American : Effects of explosions : Concrete buildings : Tunnels : Gutters : Lighting : Lightning conductors : Frictional electricity : Interiors : Barriers, etc. : Clothing : Small magazines : Thaw-houses : Tropical magazines : Ship's magazines : Naval catastrophes : Gas explosions

Construction.

In the early days of gunpowder-making special factories were not erected, but the explosive was compounded in ordinary buildings which were frequently situated in thickly populated towns, and sometimes blew up with disastrous results. As the scale of manufacture increased, it was found necessary to build powder-works in isolated places, and a special type of building was gradually evolved. It was found advisable to have the roof and at least one wall of light construction, as the force of the explosion of gunpowder is greatly reduced when the resistance offered is small; the weight of the debris projected is also diminished. For buildings in which high explosives undergo manufacturing operations it is generally considered that all the walls, as well as the roof, should be of light construction. The general principles governing the construction of danger buildings were stated by H.M. Inspectors of Explosives in *A.R.*, 1909, p. 5:

"(1) In working buildings, from which all the explosive is removed on completion of the day's work, the more flimsy the construction the better. In view of the distances to which heavy masses of debris have been thrown by explosions, the soundness of the principle is obvious. The actual material recommended is match-boarding, corrugated iron, or sheets of light fire-resisting material. For roofing, slates and tiles are dangerous, and tarred felt carries fire, so that only corrugated iron and fireproof sheets remain, and there are objections to these; in fact a good roofing material for working buildings containing explosives is much wanted.

"(2) In magazines, on the other hand, where explosive is present at all times, but where as a rule it is contained in securely closed packages, the chief danger to be anticipated is from unauthorized entry, and a substantial construction of brick, masonry or concrete is called for. An exception to this is made in the case of a factory, where a watchman is always present at night, on Sundays, and during holidays, in which case a reasonably stout corrugated iron is allowed.

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"The lining of a danger building need not necessarily be of wood. 'Neat' cement, *i.e.* cement free from sand, or any other material satisfying the conditions of General Rule No. 2,[1] may be used. In fact, in very dusty buildings a lining which can be effectively washed down by means of a hose has many advantages.

"The floor should be of soft material, such as wood or asphalt, free from grit; care being taken to fill up all interstices and crevices in which explosive dust may accumulate. Doors should open outwards and, while any one is in the building, should only be secured in such a manner as to be opened easily by a push. There should be plenty of them, and so far as practicable they should face towards the path by which a work-person would naturally endeavour to escape."

English distances.

A most important measure of safety is the requirement that magazines and other danger buildings are not allowed within certain distances of other structures or places where people are liable to be. H.M. Inspectors of Explosives have published a Table of these distances, an extract from which is given on the following pages. The distances are reduced to half in any case where the magazine or danger building is effectively screened, either by the natural features of the ground, or by good and substantial artificial mounds of such a height that a line drawn from any part of the magazine or danger building will pass through the intervening ground or mound. When a natural hill intervenes, the Inspector may permit reduction to one quarter, but in no case is the distance from his Majesty's palaces to be less than two miles. The reduction on account of mounds is only allowed in the case of quantities exceeding 1000 lb., but for mounded buildings containing 100 lb. and under, situated within the same factory, a special Table is maintained by the Inspectors, and may be seen on application. As cordite of large size has never been known to explode even when very large quantities have been burnt, it is considered to constitute a fire risk only if of size 16 or upwards and in quantities not exceeding 1000 lb.[2]

German distances.

In 1908 the German Trade Guild for Chemical Industry adopted a scale of distances for the buildings in factories for nitro-glycerine explosives: for the buildings comprising a system, the distances are generally:

Permissible quantity of explosive kg.	600	1200	2000
Distances . . . . metres	25	40	50

These distances are measured from the centre of one building to that of the other, whereas the English distances are measured from the exterior walls of the buildings. The buildings in Germany must be surrounded by earth mounds 1 metre higher than the ridges of the roofs. The distances are less

[1] *See* Guide to Explosives Act

[2] *A.R.*, 1912, p. 27.

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than those in line (2) of the English Table, even after the latter have been halved on account of the mounding of the buildings, but a direct comparison cannot be made because the method of measuring the distances is different. In washing houses for nitro-glycerine, double the above quantities are allowed for the same distances. In a magazine for nitro-glycerine 4000 kg. are allowed, and it must be at least 30 metres from any other building.

The different systems within a factory must be distant at least 80 metres from one another or from the cartridge huts, the distance being measured from the outside walls of the buildings. From the machinery buildings, laboratory and other non-danger buildings directly connected with it, the system must be distant 100 metres; and from the offices, gun-cotton works, engineers' shops and other non-danger buildings not connected with it, the distance must be 250 metres. The following Table gives the distances for the other danger buildings of a factory for nitro-glycerine explosives:

	Distances Centre to centre		Limit for explosives	Limit for workers
	metres		kg.	No.
Cartridge huts for high per cent. explosives.	12		50	2
	15		75	
Cartridge huts for low per cent. explosives .	15		200	4
Packing houses	30		No accumulation	6
Magazines for explosives	From one another	From the packing-houses		
	15	40	5,000	—
	40	150	30,000	—
Drying house for collodion cotton . .	45		—	2

High per cent. explosives are those that contain 25 per cent. nitro-glycerine or more, low per cent. ones contain not more than 5 per cent.

Austrian distances.

In Austria-Hungary distances from magazines and laboratories have been laid down in the regulations for the care of material.[1] The objects, from which distances are specified, are divided into two classes: class 1 comprises buildings in which there is no fire, and roads and paths that are little used, and factory buildings not directly devoted to manufacture; class 2 comprises all buildings, railways, roads and paths, where the results of an explosion might be disastrous.

[1] *See S.S.*, 1910, p. 177.

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DISTANCES FOR MAGAZINES AND

The figures in brackets are the distances to be observed when gunpowder

When such distances are assigned, 2 lb. of manufactured fireworks or ½ lb. of

Amount of explosives to be allowed in the magazine or danger building		500	1000	2000	3000
(1) Room in connection with the magazine, for filling cartridges for small-arms (in which 5 lbs. of explosive is allowed unloaded: section 46 of Act)	yards	50 (35)	50 (35)	50	51
(2) Mineral or private railway; highway or other open place of resort; canal, reservoir, etc.; workshop in connection with magazine for preparing charges for blasting (in which 100 lbs. gunpowder or 50 lbs. of other explosive may be present: section 47); buildings and magazines inside the same factory; two or more magazines belonging to the same occupier, or by mutual consent of the respective occupiers	,,	50 (35)	75 (50)	100 (75)	101 (90)
(3) Other magazine or store for explosives, or room or workshop in connection therewith; furnace, kiln, or fire for the use of any boiler, engine, or machine, or for any manufacturing purpose	,,	100 (65)	150 (100)	200 (150)	200 (175)
(4) Public railway	,,	100 (65)	150 (100)	200 (150)	210 (175)
(5) Dwelling house *with* the consent in writing of the occupier	,,	50 (35)	75 (50)	100 (75)	110 (90)
(6) Dwelling-house *without* such consent; factory not belonging to Government; Government factory or magazine with consent; theatre or other building, where people are accustomed to assemble	,,	100 (65)	150 (100)	200 (150)	240 (175)
(7) Government factory or magazine without consent	,,	880 (585)	1320 (880)	1760 (1320)	1780 (1540)
(8) Palace or house of residence of His Majesty, his heirs and successors	miles	2	2	2	2⅛

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OTHER DANGER BUILDINGS

or cordite in cords not contained in metal cases only are stored.

any other explosive may be reckoned as equivalent to 1 *lb. of gunpowder.*

4000	5000	6000	7000	8000	9000	10,000	10,000 to 100,000 lb.
52	52	53	53	54	54	55	50 + ·0005 c. where c is the quantity of explosive
102	104	105	106	108	109	110	100 + ·001 c.
200	200	200	200	200	200	200	150 + ·005 c. up to 20,000 lb. 100 + ·0075 c. 20,000 to 100,000 lb.
215 (200)	225 (210)	235 (220)	240 (230)	250 (245)	255	265	200 + ·0065 c.
120 (100)	130 (110)	140 (125)	145 (140)	155 (150)	165 (160)	175	100 + ·0075 c.
280 (200)	320 (255)	365 (310)	405 (360)	445 (415)	485 (470)	525	200 + ·033 c.
1805 (1760)	1825 (1790)	1850 (1820)	1870 (1850)	1890 (1880)	1910 (1905)	1930	1760(1 + ·0001 c.)
2¼	2¼	2⅜	2½	2½	2⅝	2¾	2 + ·00008 c.

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	Capacity	Class 1	Class 2
		Distance in metres	
Powder or explosive magazine . . .	Up to 100 kg.	100	100
,, ,, ,, . . .	100–1000	200	300
,, ,, ,, . . .	1000–3000	300	500
,, ,, ,, . . .	over 3000	400	750
Shell magazine	No limit	200	400
Small arm ammunition magazine . . .	No limit	50	50
Laboratories in which explosives are dealt with	—	200	300

These distances may be diminished if effectual protection is afforded by mounds, trees or natural features of the ground. The rules do not apply to military magazines. The distances are greater than the corresponding ones in the English Table.

American distances.

In 1910 a committee of American manufacturers, with the assistance of the Chief Inspector of the Bureau of Explosives, made a study of all the recorded explosions throughout the world, and from the results drew up a Table, which has been adopted officially in the United States for explosives magazines.

Pounds of explosives	Inhabited buildings (feet)	Public railway (feet)	Pounds of explosives	Inhabited buildings (feet)	Public railway (feet)
50	120	70	10,000	890	535
100	180	110	20,000	1,055	635
200	260	155	30,000	1,205	725
300	320	190	40,000	1,340	805
400	360	215	50,000	1,460	875
500	400	240	60,000	1,565	940
600	430	260	70,000	1,655	995
700	460	275	80,000	1,730	1,040
800	490	295	90,000	1,790	1,075
900	510	305	100,000	1,835	1,100
1,000	530	320	200,000	2,095	1,255
1,500	600	360	300,000	2,335	1,400
2,000	650	390	400,000	2,555	1,535
3,000	710	425	500,000	2,755	1,655
4,000	750	450	600,000	2,935	1,760
5,000	780	470	700,000	3,095	1,855
6,000	805	485	800,000	3,235	1,940
7,000	830	500	900,000	3,355	2,015
8,000	850	510	1,000,000	3,455	2,075
9,000	870	520			

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These distances are for magazines that are "barricaded," that is, screened from other buildings or railways by either natural or artificial barriers. Where such barriers do not exist, the distances shown should be at least doubled. A comparison of the English with the American Table of distances shows that the latter requires greater distances for the smaller quantities of explosives, whilst the English Table requires greater distances for the larger quantities, but does not contemplate that more than 100,000 lb. will be placed in one magazine.

Effects of explosions.

Experiments have been carried out at various times and places to ascertain the distances at which explosions will produce a specific effect according to the quantity of explosive. Such experiments have been performed at Kummersdorf in Germany, and at Arendonck and Bewerloo in Belgium, and in 1902 to 1904 an extensive series was carried out in France.[1] In the French experiments different quantities of various explosives were exploded in the open, and at various distances a number of little screens were erected, so arranged that the same degree of force would cause each of them to fall back. It was thus possible to ascertain the distances at which the same effects were produced. The most simple theory would lead one to expect that the distance would be proportional to the square root of the weight of the charge. These experiments, which were carried out with quantities of 0·1 to 100 kg. of melinite, 150 kg. of cheddite, and 300 kg. of gunpowder were in agreement with this theory. They were confirmed by trials in which small huts with glass windows were exposed to the effects of the explosions at various distances. This rule is expressed by the equation $d = k.\sqrt{c}$, where d is the distance, and c the weight of explosive, and k a constant depending on the nature of the explosive and the sort of damage considered. For high explosives causing the breaking of window panes and slightly injuring the frames and wooden walls $k = 10$ about, the distances being measured in metres and the charges in kilogrammes. Up to 30,000 lb. this equation gives greater distances than those in line (6) of the English Table, but above that quantity it gives smaller distances. With gunpowder double the quantities are required to produce the same effects, or $k = 7$. This is in agreement with the English Table up to quantities of about 2000 lb.

Lheure also determined the velocity with which the impulse is transmitted through the air. Near the seat of the explosion the velocity is much greater than the normal velocity of sound, but it falls off rapidly and, at about the distance at which window-panes are no longer broken, the velocity is the same as that of sound. The more brisant the explosive the greater is the initial velocity of the impulse. Increase of the quantity of explosive does not seem to increase the initial velocity, but it causes the rate of diminution to be less.[2]

[1] *See* Lheure, *P. et S.*, vol. xiii., p. 161 ; *S.S.*, 1907, pp. 228, 249, 308, 427, and 446.

[2] *See also* Comey's experiments, p 351.

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The figures in the American Table do not agree very well with an equation of the above form. For small quantities the distances are more nearly proportional to the cube root of the weight of explosive, and for very large quantities the variation of the distance is more nearly proportional to the increase of the weight. It is somewhat doubtful whether the equation really represents the results obtained under practical conditions. The records of explosions do not indicate that any distinction should be drawn between gunpowder and high explosives, when quantities of several tons are concerned.

When black powder explodes in a magazine, the structure offers so much less resistance than the ground, that nearly all the energy of the powder is expended in an upward or sideward direction, even though the magazine be of strong construction. When a high explosive detonates, a larger proportion of the energy is expended in a downward direction, because the time occupied by the explosion is much shorter, and the air offers considerable resistance to the almost instantaneous evolution of gas. Consequently, when a large quantity of nitro-glycerine or other high explosive goes off, a severe wave of concussion is transmitted through the earth at the same time as waves are sent through the air. Guttmann has laid great stress on the earth waves,[1] but except in the case of an underground building the energy expended on the air must be greater than that expended on the ground, and consequently most of the damage done by an explosion is due to the air-wave. That this is so is confirmed by the fact that the provision of a mound round a danger building reduces the area of destruction to about half, for the mound can only give protection against air-waves and flying missiles. In the case of explosions in nitro-glycerine factories, the earth-wave is often much reduced by the fact that the tanks containing the explosive do not rest upon the ground, but are supported some distance from it on a staging. Guttmann has suggested that danger buildings should be built over pits in order to reduce the concussion of the earth.

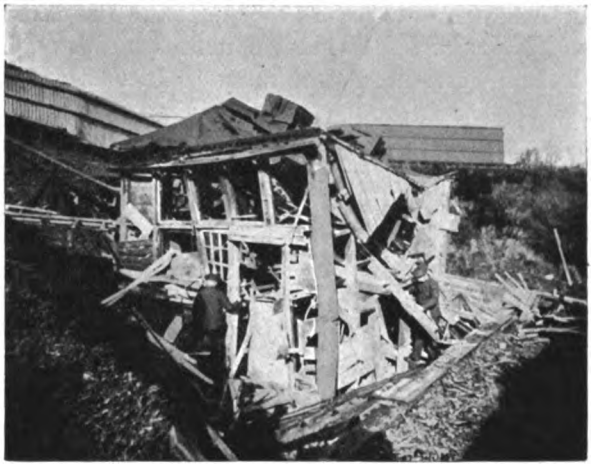

FIG. 122. Building Wrecked by Explosion 30 yards away. Ardeer, February 27, 1897

[1] *J.S.C.I.*, 1908, p. 669 ; *S.S.*, 1908, p. 266.

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It is noticed that in buildings near the seat of an explosion the windows and doors are blown in, but at greater distances they are sucked out, so that the broken glass, for instance, all lies outside the building. This difference is shown by the two photographs (Figs. 122, 123) taken from Guttmann's paper. The first shows the crushing in of a nitro-glycerine separating house distant 30 yards from the site of the explosion of 1800 lb. of nitro-glycerine, and the other the sucking out of the walls of a building situated 145 yards from a glazing house in which 7000 lb. of gunpowder exploded.

The gases formed in the explosion are only projected to comparatively small distances. In the Faversham explosion of February 21, 1879, where the conditions were peculiarly favourable to their projection laterally, the scorching effect did not extend beyond 50 yards,[1] whereas serious structural damage was done at 283 yards, and windows were broken at a distance of a mile. A wave of compression is set up, which travels through the air in all directions, and is immediately followed by a wave of rarefaction, or rather there is a complete wave which consists, like an ordinary sound-wave, of compression followed by rarefaction, and this is followed by other similar waves each more feeble than its predecessor. As the waves travel away from the place of origin, the compression part of the wave becomes shorter and the rarefaction portion longer, so that beyond a certain distance the effects of the latter exceed those of the former.

FIG. 123. Building Wrecked by Explosion 145 yards away. Faversham, February 21, 1879

The direction in which the air-waves can do least damage is the upward one. Hence the desirability of having a light roof and surrounding the danger building with substantial mounds. But unfortunately the light roof introduces other dangers, for if one of the other buildings in the factory be blown up, a piece of machinery, or of the building, may be projected right through the roof and cause the explosive within to go off too. There have been several instances in which the extent of a catastrophe has been greatly increased in this way. It is partly on this account that magazines are usually built with

Concrete buildings.

[1] *S.R.*, No. 22, p. 7.

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substantial walls and roofs. In the experiments carried out at Kummersdorf in 1897 and 1899 quantities of 1500 and 500 kg. of gelatine dynamite were exploded in small magazines constructed specially of fine gravel concrete, and it was found that this material was entirely broken up, so that no large masses were projected about. On the other hand, in some experiments carried out in France, in which quantities of 25 kg. of Dynamite No. 2 were exploded within small magazines made of concrete, armoured and unarmoured, it was found that considerable pieces were projected 50 metres, and smaller fragments 75 metres.[1] The difference from the results obtained in Germany may have been due to some difference in the composition of the concrete. Safety is further increased by covering the magazine with a layer of earth, which will arrest any considerable pieces of the fabric. For new magazines erected in Germany for the storage of high explosives this method of construction is now generally adopted (*see* Fig. 124). They are made of gravel concrete without any admixture of sand. The walls are at least 60 cm. (2 feet) thick, the roofs are vaulted and covered with a layer of earth at least a metre thick. There are double doors, of which the outer is of oak at least 5 cm. (2 inches) thick.

In an explosion of 700 or 800 kg. of Gelignite, which occurred in 1907 at the Carbonite Works at Schlebusch, a magazine of this sort, distant only 60 metres from the explosion, was not injured in any way.

Guttmann proposed to construct all the danger buildings of factories for high explosives of armoured concrete with walls 20 cm. (8 inches) thick, containing iron tie-rods 6 to 12 mm. ($\frac{1}{4}$ to $\frac{1}{2}$ inch) in diameter.[2] The roof also was to be of concrete, but double, with a layer of sand 36 cm. (1 foot 5 inches) between, in order to arrest any missile which penetrated the outer layer of concrete. At the 7th International Congress of Applied Chemistry held in London in 1909 Bichel objected to this method of construction on the ground that it is too heavy and too unstable.[3] Subsequently Guttmann adopted another method for the construction of the roofs of these danger buildings ;[4] he made them of light but strong wooden beams protected above and below with expanded metal or wire netting, the whole being covered with corrugated iron to keep out the rain. Such a roof offers great resistance to objects falling upon it.

Bichel also has constructed danger buildings of armoured concrete, but he covers them entirely with earth except on one side, which consists mostly of glass.[5] The general design is very similar to that of the

[1] *P. et S.*, vol. xv., 1910, p. 177.
[2] *J.S.C.I.*, 1908, p. 669 ; *S.S.*, 1908, p. 266.
[3] *See* Report of Section III B, p. 49.
[4] *J.S.C.I.*, 1910, p. 930 ; *S.S.*, 1910, p. 265 ; Eng. Pat., 4094 of 1909.
[5] *Loc. cit.* ; *also S.S.*, 1910, p. 182 ; *Chemische Industrie*, 1912, p. 139.

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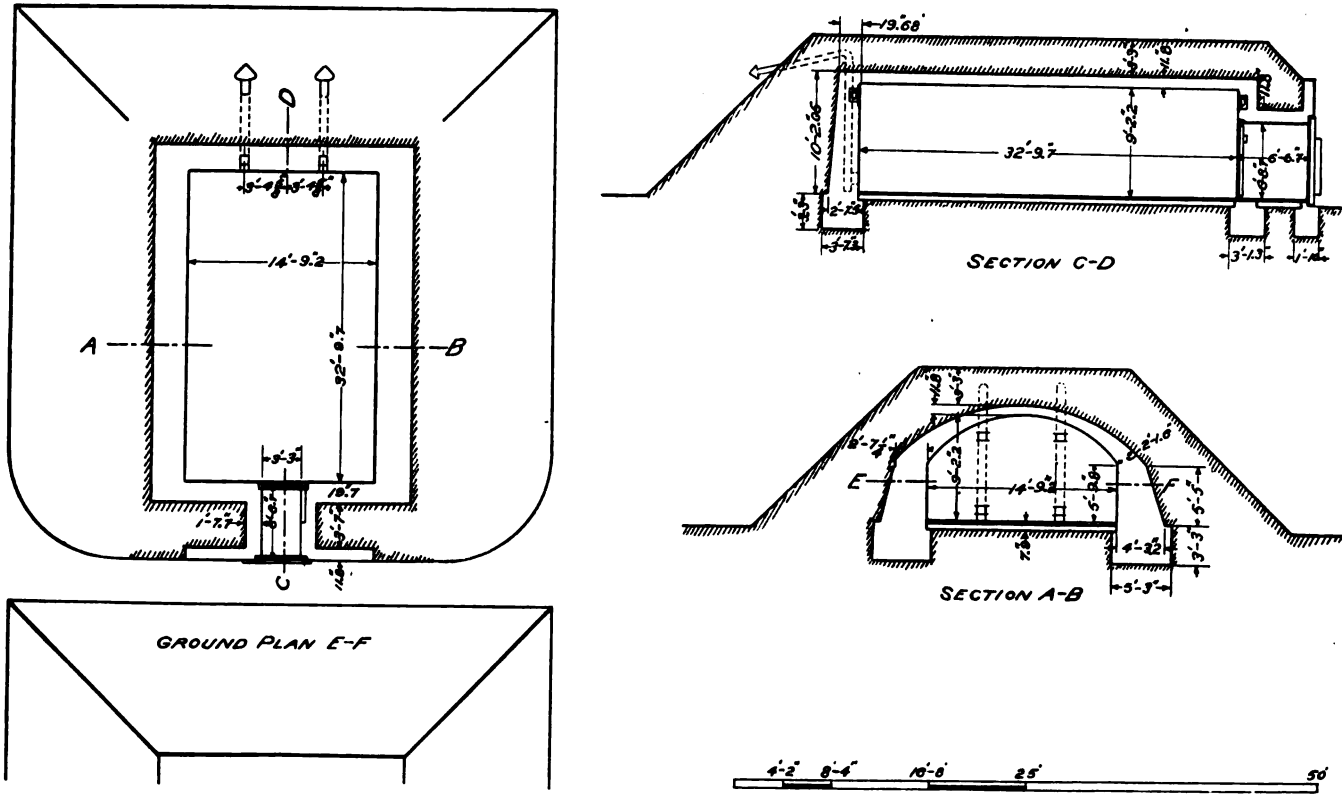

FIG. 124. Magazine of Carbonite Explosives Co., Schlebusch
(From *Bureau of Mines Technical Paper*, No. 18)

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magazine shown in Fig. 124, but inside the vaulted roof made of fine gravel concrete, there is another roof 8 cm. thick made of armoured concrete, with an air space of 4 cm. between the two. In front of the glass side of the building there is a high mound, a short distance away, through which access is provided to the building by means of a short straight tunnel. The mouth of this tunnel is protected by means of another mound. It has been found that a long tunnel leads to the formation of a very long flash in the case of an explosion, and making the tunnel with a bend in it does not add to the safety, but is liable to cause the tunnel to collapse.

Tunnels.

Danger buildings in which large quantities of explosive are dealt with should never be connected directly with one another by tunnels or passages. The gutters for the conveyance of nitro-glycerine from one building to the next are also a source of danger. They should be connected to the plant at either end only by rubber tubes, which should be disconnected except when nitro-glycerine is actually being transferred. The gutters should be covered over by thin canvas only, to avoid the communication of explosion from one building to the other by means of long flames. Perhaps it would be better not to have them covered in, but merely protected by means of a roof raised some distance above the edges.

Gutters.

Lighting.

For the artificial lighting of buildings in explosives factories electricity is used almost universally. Electric incandescent lamps are used mounted in the walls in recesses separated from the interior of the building by a thick pane of glass. All the wires and connexions are outside the house. In the case of magazines electric current is not always available; lamps containing candles or burning rape oil should then be used, and they should be mounted in the walls in recesses that can only be opened from outside the building. For portable lights electric hand-lamps or electric torches are best, but for magazines where the explosives are in packages rape oil or candle lamps are used sometimes.

Lightning conductors.

Some danger buildings and all magazines, except those which contain only very small quantities of explosive, must be provided with lightning conductors. In spite of all that has been written on the subject most architects, engineers and builders seem to think that effective protection against lightning is provided by running a copper tape or rope up a building and connecting it with a metal point fixed on to the ridge of the roof. The lightning is expected to follow obediently all the turns and twists in the conductor, and never to spring across and take short cuts, which, however, is just what it always does. The vast majority of the lightning conductors are calculated rather to conduct the lightning into the building than away from it. Fortunately, severe thunderstorms are rare in England and many other countries, and so the futility of these appliances is not rendered evident. In South Africa and in some parts of Germany the same immunity is not enjoyed, and a number of catas-

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trophes have led to much careful thought being given to the subject of protection from lightning.

Nitro-glycerine factories are specially liable to be struck. The top of the nitrating house is necessarily raised a considerable height above the lower portions of the system, and the large masses of metal within the house add to the danger. Moreover, a comparatively small spark, which would do no serious damage in an ordinary building, will suffice to explode the nitro-glycerine, so that a building may be blown up without being struck directly. If the lightning strike the ground near by, it may set up such powerful induced currents that the nitro-glycerine will be exploded. In 1895 Major Cardew drew up an elaborate scheme for the protection of nitro-glycerine factories in South Africa.[1] On each side and at the ends of each line of buildings to be protected, hollow iron pillars about 40 feet high were to be erected, their lower ends being sunk about 10 feet in the ground. To counteract the extreme dryness of the soil perforated water-pipes were to be led up into each of the pillars so that, when deemed advisable, the pillars themselves and the earth at the base might be thoroughly drenched to reduce the resistance of the earth. Circles of points were to be fixed to the pillars at intervals of 10 feet or so. The buildings themselves were, if practicable, to be of galvanized iron sheets, but if this could not be done, a screen of iron wire netting was recommended. It was suggested that this netting should be supported by wire ropes attached to short iron poles on the mounds, these short poles being provided with points, and being connected by means of stout wire rope to the above-mentioned high pillars.

As regards the masses of metal in the buildings and the pipes leading into them, it was pointed out that the danger is twofold: either they may be charged inductively, with the consequence that sparks will pass when the flash occurs, or they may act as alternative paths for the whole or part of the flash. The first of these contingencies may best be provided against by thoroughly "earthing" each separate piece of metal, and the second by electrically connecting all masses of metal to one another and to the protecting system, or by separating them by so large a gap as to eliminate the risk of communication. It was pointed out that it is not even safe to have sharp portions of two metal masses very close together, although the masses themselves may be connected by a metallic conductor. Pipes entering the buildings should be thoroughly connected to the protecting system, and if practicable insulated by rubber tubing or otherwise from the contiguous walls of metal.

Practically the same system of protection against lightning was adopted officially in Germany in 1906,[2] with a few modifications. The pillars in the outer zone were not so high, but from them was suspended a complete network of wires, which stretched all over the building at a height of about

[1] *See S.R.*, No. 179.

[2] *See S.S.*, 1907, p. 109.

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3 metres above the roof. A second network was laid immediately on the roof. This system of double networks is called the Faraday cage, from a laboratory experiment devised by the great investigator. It has been adopted in South Africa also, but both there and in Germany buildings have been struck and destroyed, although they were provided with this very elaborate system of conductors. In June 1910, three buildings were blown up simultaneously by lightning at the Schlebusch factory,[1] and in the same year the Faraday net failed in another German factory also. In February 1911, there was a similar catastrophe at Modderfontein, whereby five men were killed. These disasters have brought into disrepute the system of suspending wires over the top of a building, because they appear to lead the flash into the house rather than away from it, as has been shown experimentally by Rinckel [2] and Hagen.[3] The prevailing opinion now is that the best protection is afforded by plain metal masts at some little distance from the building. These masts can be made at a small cost from ordinary gas-piping ; they should be fitted at the top with metal points to assist the dissipation of induced charges of electricity.

It is a rule that the lightning conductors of danger buildings must be tested for electrical resistance at regular intervals to ensure that there is no break in the contacts. A direct flash of lightning can, of course, spring across enormous gaps, so that a small discontinuity in the conductor would probably be far less harmful than a sharp turn, but another function of the conductor is to dissipate gradually the induced charges that form on the surface of the earth when a thunder cloud passes over it, and for this purpose continuous electric contact is essential.

It is expected by Bichel that the underground nitro-glycerine houses at Schlebusch will be far less liable to be struck by lightning.

Frictional electricity.

Dangerous charges of electricity may also be formed by the friction of non-conducting materials. The belts used for driving incorporating machines, for instance, are liable to become strongly electrified, especially in dry weather. To prevent this, at Walham Abbey, the belts are dressed once a week with a mixture of glycerine and water, which makes the belts conduct and so prevents the accumulation of static charges of electricity. Dry gun-cotton is a material which is very liable to become electrified. All plant, on or in which it is placed, should therefore be connected to earth.

Interiors.

The interior of danger buildings must be so constructed that so far as possible no iron or steel or gritty material is exposed. The thoroughness with which this rule is carried out depends to some extent on the nature of the explosives and of the operations to be carried out in the building. In nitro-glycerine houses the floors are generally made of lead sheet joined together

[1] *See A.R.*, 1910, p. 38.
[2] *S.S.*, 1911, p. 141 ; 1907, pp. 109 and 277.
[3] *S.S.*, 1911, p. 162.

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by burning, and the walls are of wood. In gun-cotton stoves and mixing houses, and other buildings in which explosive dust is liable to be formed, the walls and roof should be made so that they can be washed down with a hose, and should have no crevices in which material can lie. A smooth lining of zinc sheets soldered together serves the purpose well. In other buildings, and in magazines, the walls are generally lined with wood, and the floor is made of the same material; all crevices must be filled up; the nails used should be of copper, brass or other alloy; if iron nails or screws are used, they must be counter-sunk and covered with putty. Linoleum makes a very good covering for the floor, but it must be so laid that explosive dust cannot accumulate underneath it. Perhaps the very best material for the floor of ordinary danger buildings and magazines is asphalt, provided it be properly laid. Walls may also be made of neat cement painted over.

Barriers, etc.

To prevent the introduction of grit into magazines and other danger buildings, the workers must change their boots as they enter, and in order that there may be no doubt as to which part is "clean" and which "dirty," there must be a wooden barrier erected, about 9 inches high, at the entrance to the building. Just outside the barrier there should be a lobby or porch in which the boots can be changed, and a small "clean" board on which the clean boots can stand whilst they are being put on. This board may with advantage be fastened with a hinge so that it can be tipped up when not in use. Those who have occasion to visit the danger building for only a short time usually put on clean over-boots with rubber soles, or preferably made entirely of rubber. The boots worn by the workers should also have soft soles with no iron nails. In some cases it has been found advisable to have copper rivets in the boots so as to "earth" the worker electrically, and so prevent the formation of sparks when he is dealing with substances like dry gun-cotton, which are liable to become electrified. In gun-cotton stoves, however, it is better not to wear any boots or shoes at all but only an extra pair of woollen socks. In the East the natives as a rule go bare-foot, especially when indoors, consequently it is not necessary to provide special foot-gear for them to wear when they work in danger buildings, but a tub of water is placed just outside the barrier, and into this they have to dip their feet before entering the building, so as to wash off the grit.

Clothing.

All workers in danger buildings must wear special clothes which have no metal buttons or other metal parts, and no pockets. Where there is any danger of fire, the clothes should be made of wool, or be treated so as to render them uninflammable. The clothes should not be allowed to become impregnated with explosive or combustible material. The lives of the workers may be jeopardized if these precautions are not observed. Due provision must be made, by searching or otherwise, that no matches, pipes or other dangerous articles are introduced into a danger building.

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Small magazines. The principal regulations in force in England for small and moderate-sized stores and magazines for explosives are given in Appendix E of the *Guide to the Explosives Act.* Messrs. Curtis's and Harvey have recently issued a pamphlet, showing how these regulations can be carried out effectively and inexpensively, and giving full and detailed instructions for the erection of the buildings. The U.S. Bureau of Mines has also given instructions for the erection of magazines in the *Primer on Explosives for Coal-Miners* (Washington, 1911), and in Technical Paper 18 on "Magazines and Thaw-Houses for Explosives" (Washington, 1912), and the Du Pont Co. have given illustrations of buildings in their pamphlet on "High Explosives." The Bavarian Government also has issued instruction concerning this matter.[1]

Thaw-houses. Thaw-houses are required for thawing frozen nitro-glycerine explosives, when they have become frozen. In America the thawing is often carried out by placing the case of explosive within a closed box, which is embedded in fresh stable manure. This method of thawing is rather slow, however, and the temperature may rise to a dangerous height, 150° F., for instance. If practicable, the explosive should be warmed in a special house heated to about 100° F. (38° C.) by means of warm-water pipes, which preferably should not be brought into the building itself, but placed in a low recess just outside, communicating with it by means of an opening at floor level. It is still better not to allow the explosive ever to become frozen, but to keep the magazine itself at a temperature of 15° or 20° C. winter and summer.

Tropical magazines. In hot climates explosives containing nitro-cellulose or nitro-glycerine should be kept as cool as possible, because at high temperatures they deteriorate rapidly. This applies especially to the smokeless powders used for military and naval guns, as they have to be stored for much longer periods than commercial explosives. The magazines should therefore be specially constructed so as to keep as cool as possible, especially during the hot weather. If constructed of heavy masonry there is very little variation of temperature during the twenty-four hours, and this is of advantage. The magazine should only be ventilated during the night or the very early morning, when the temperature of the external air is lowest. In places where there is a large annual range of temperature considerable advantage is obtained by covering the magazine with earth as in Fig. 124. Where the quantities of explosive stored are sufficiently large, the magazines may with advantage be kept cold artificially, by circulating through them air cooled by means of a refrigerating plant. When this is done, the magazine must be insulated thermally by means of a layer of about 6 inches of slag wool or other suitable material applied to the walls, ceiling and floor.

Ship's magazines. On board ship the explosives carried must necessarily be in close proximity to the crew and the other cargo. A wooden compartment is constructed well

[1] *See S.S.*, 1911, p. 35.

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away from the boilers, steam-pipes, and all materials that could have an injurious effect.[1] On war-ships there are, of course, regular magazines forming part of the design of the vessel. There have been a number of cases in which ships have been destroyed by the spontaneous ignition of the smokeless powder on board, and since the *Jéna* catastrophe in 1907 practically all war-ships have had their magazines kept cold by means of refrigerating plant.

Naval catastrophes.

One of the most serious dangers to be guarded against in the storage of explosives is spontaneous ignition. Fires due to the ignition of deteriorated smokeless powders have been fairly numerous. Some of those that have occurred on board war-ships have been very disastrous. In September 1905, the Japanese battleship *Mikasa* was destroyed in this manner in Sasebo harbour, and 599 lives were lost. The Brazilian war-ship *Aquidaban* sank in the port of Jacare, Rio de Janeiro, in January 1906, with the loss of 213 lives. The French battleship *Jéna* blew up in March 1907, in Toulon harbour, killing 114 men. Another Japanese ship, the *Matsushima*, was lost off the Pescadores in March 1908, together with 141 lives, apparently in consequence of the spontaneous ignition of the cordite on board. The French battleship *Liberté* was entirely destroyed in Toulon harbour in September 1911, and 204 men were killed, 136 injured severely, and 48 slightly. These catastrophes are only some of the most serious. In addition there have been very many other cases of ignition, which, however, have fortunately not extended to the whole of the contents of the magazine, and consequently the damage has not been so serious. There have also been many cases of spontaneous ignition in magazines on land: in some cases the magazines have been entirely destroyed, together with surrounding objects; in other cases the ignition has not spread, and the damage has been trifling. A study of these cases leads to important conclusions as to the precautions to be taken to prevent a spontaneous ignition of smokeless powder leading to a destructive explosion. The total destruction of the *Jéna* was due to the spread of the flames from a magazine containing smokeless powder (Poudre B), which had ignited spontaneously, to one containing black powder, which then exploded. The loss of the *Matsushima* was apparently due to the same cause, and explosions of land magazines have in some instances been brought about in the same way, as, for instance, that of Batuco in Chile in March 1908.[2] Gelatinized smokeless powders themselves hardly ever explode unless very strongly confined, and the larger sizes, which are used for ordnance, will only burn, however fierce the heat may be. The first deduction is therefore that smokeless powders should be stored quite separately from black powder and all other explosives that are liable to explode when ignited. Gunpowder is no longer used for the propulsive charges of naval guns, so that no ships can in future be destroyed

[1] *See* Memorandum of the Board of Trade relating to the Carriage of Dangerous Goods and Explosives in Ships.

[2] *See S.S.*, 1909, p. 265.

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in exactly the same way as the *Jéna* and the *Matsushima* were. The explosion on the *Liberté* was, however, much more violent, and men were killed several kilometres away by flying debris. There can be no doubt that this was due to the intense conflagration of the smokeless powder having caused the detonation of the high explosive shell filled with Mélinite (picric acid). Unfortunately it is not always possible on board ship to keep the shell very far away from the powder magazines, and consequently reliance must be placed on other precautions—refrigerating the magazines and thorough periodical inspection of the powder.

Gas explosions. Although there is no recorded case where smokeless powder has itself exploded after igniting spontaneously in a magazine, yet in a number of instances the ignition has been accompanied by explosive phenomena of a comparatively mild kind. When smokeless powder deflagrates in the absence of air, the products consist largely of combustible gases. Berthelot gives the following figures for the products formed when nitro-glycerine and gun-cotton are ignited by means of a hot wire, and allowed to burn at a pressure about equal to that of the atmosphere : [1]

	Nitro-glycerine	Gun-cotton
NO	48·2	24·7
CO	35·9	41·9
CO_2	12·7	18·4
H_2	1·6	7·9
N_2	1·3	5·8
CH_4	·3	1·3
	100	100

The composition of the products will, of course, depend on that of the powder and also of the resistance offered by the package, that is, of the pressure under which the deflagration proceeds, but there will always be a large proportion of combustible gases, and these when they mix with the air of the magazine form an explosive mixture, which may be ignited by coming in contact with the burning contents of the case. In some cases the effects can only be explained by assuming that a gas explosion occurred. Similar phenomena have been observed, when spontaneous ignitions have occurred in stores of celluloid, the principal constituent of which is nitro-cellulose, and Will has come to the same conclusion as to the cause.[2] Those who have to do with the storage of gelatinized smokeless powders should therefore bear in mind that in the case of a spontaneous ignition far more serious damage may be caused by a gas explosion than by the ignition itself ; moreover, if other explosives are stored in an adjoining compartment, the gas explosion, by blowing down

[1] *Explosives and their Power*, pp. 283, 289.
[2] *See Mitteilungen aus der Centralstelle*, Heft 5, Feb. 1906.

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the partition between, may lead to the explosion of these explosives, and so produce a widespread disaster. In the confined space on board ship such a gas explosion is likely to have very serious results. In the very full reports concerning the *Jéna* disaster there is distinct evidence that there was a gas explosion before the black powder went off. It might, perhaps, be possible to guard against the results of such an explosion on board war-ships by making the magazines of such strength that the walls, floors and roofs would withstand the pressure produced.

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CHAPTER XXXIV

STABILITY

Rate of decomposition : Stabilizers : Ureas : Amines : Mineral jelly : Phenanthrene : Amyl-alcohol : Aromatic ethers, etc.

Rate of decomposition.

THERE is no problem connected with modern explosives more important or more elusive than that of their stability. Black powder, and other similar mixtures of inorganic nitrates with combustible materials, can be stored indefinitely without suffering perceptible deterioration, provided that they are kept dry ; picric acid, nitro-toluenes and other aromatic nitro-compounds are also very permanent. Nitro-celluloses, nitro-glycerine and similar substances, on the other hand, decompose to a perceptible extent even at the ordinary temperature, and the rate of decomposition increases rapidly with rise of temperature. The researches of Will [1] and Robertson [2] have established the fact that there is a certain minimum rate of decomposition of nitro-cellulose depending on the temperature and the degree of nitration. The presence of certain impurities in the nitro-cellulose may increase this rate considerably, but no amount of purification will reduce it below the "limit rate." The presence of oxides of nitrogen accelerates the decomposition, hence it is necessary to remove them as fast as they are formed by a current of inactive gas, when the rate is being determined. Sulphuric and other acids also act as catalytic agents in accelerating the reaction.

To express the variation of the rate of decomposition with temperature Will proposed the formula $log\ N = a + b \times 0{\cdot}9932^t$, and for the nitro-cotton with which he was experimenting he found $a = 8{\cdot}842$ and $b = -22{\cdot}86$, N being the number of milligrammes of nitrogen evolved by 2·5 g. in ¼-hour. But the facts are represented equally well, or better, by the simpler equation

$$log\ V = Kt + C$$

or

$$V = k^t \times c,$$

where V is the velocity of the reaction, t the temperature, k and c constants, and K and C their logarithms. Equations of this form were suggested by

[1] *Mitteilungen aus der Centralstelle*, Heft 2, Dec. 1900, and Heft 3, July 1902.

[2] *J.S.C.I.*, vol. i., 1902, p. 828.

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Berthelot many years ago.[1] The constant K depends upon the state of purity of the substance, the degree of nitration and the units in which the velocity V is measured. K depends only on the nature of the substance. For nitro-cotton, according to Will's results, the rate of decomposition is doubled for every rise of 5° C. Therefore $K = \frac{log\ 2}{5} = 0{\cdot}0602$, and $k = 1{\cdot}149$.[2] Robertson obtained the same value in the case of nitro-glycerine.

Gelatinized nitro-glycerine high explosives are liable to deteriorate in this way, and in several instances the blowing up of magazines has been traced to this cause. Many consignments of such explosives have been condemned after shipment from this country to Australia on account of their failure to pass the heat test imposed by the inspectors. But it is in connexion with smokeless powders for military and naval use that most attention has been drawn to the gradual deterioration of these explosives, and their liability to ignite spontaneously. Some of the principal disasters due to this cause were mentioned in the last chapter. As regards the variation of the rate of deterioration with temperature, the French authorities have adopted the rule that an hour at 110° is equivalent to a day at 75° and a month at 40°,[3] which gives values for K of 0·0394 and 0·0423. On the other hand, in a British War Office publication, the *Regulations for Army Ordnance Services*, Pt. II, paragraph 359, 1908, a Table is given based on an increase in the rate of deterioration for every 5° C. of 1·7 times, which gives for K a value of 0·0461. The French figures are for nitro-cellulose powder, whereas the English ones are for cordite, and they have been deduced from data of quite a different kind, so that a close agreement could not be expected in a matter in which it is so difficult to attain accuracy, but it seems to be clear that the rate of deterioration is less than doubled for a rise of 5° C.

The rate of deterioration or, in other words, the magnitude of the constant, C, depends upon the presence or absence of various substances in the smokeless powder or other explosive. Normal nitro-cotton thoroughly purified in accordance with the methods given in Chapter XIII deteriorates less rapidly, and therefore is more stable, than the nitric esters of allied substances such as oxy-cellulose or pecto-cellulose. Some of the unstable products are removed by treating the nitro-cellulose with alcohol.

The rate of deterioration is increased by the presence of strong acid, which hydrolyses the compounds. The acid is not consumed in the reactions that occur, on the contrary the explosive becomes more and more acid by the formation of nitric acid. The reaction is therefore auto-catalytic. The

[1] *Ann. Chim. Phys.*, 1862, p. 110.
[2] *Seventh Inter. Cong. Appl. Chem.*, 1909, vol. iii*b*, p. 95.
[3] *P. et S.*, vol. xv.

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reactions that occur during the storage of smokeless powders are very complex : the solid and liquid products formed were discussed in Chapter XIII, but the mechanism of the change is apparently dependent very largely on the presence of the oxides of nitrogen, which are gases. It was found by Robertson and Napper [1] that of the nitrogenous gases evolved by gun-cotton at 135° under the conditions of the Will test, about 40 per cent. consists of nitrogen peroxide NO_2, and the remaining 60 per cent. is mostly nitric oxide NO. From nitro-glycerine the whole of the nitrogen is evolved in the form of NO_2.[2] If the gaseous products remain in contact with the gun-cotton, the NO_2 is reduced to NO, and the gun-cotton is correspondingly oxidized with evil effects on its stability. Nitro-glycerine is apparently not oxidized so readily, and this may be one reason for the greater stability of nitro-glycerine powders. If air be present, the NO is at once oxidized again to NO_2, and unless the nitrous gases are removed in some way, these oxidations and reductions will continue until all the oxygen present has been exhausted. This oxidation of nitro-cellulose proceeds most rapidly if the conditions be such that there is a continuous but small supply of oxygen : if the uncompressed material be exposed freely to the air, the nitrous oxides diffuse away before they have been able to do much harm. Thus it has been observed that if porous nitro-cellulose be compressed into compact blocks under a pressure of 3600 kg. / square cm. (23 tons per square inch), and heated at 110° under the conditions of the Vieille test, it gives a result of only about 10 hours, whereas the same material merely moulded under a pressure of 400 kg. / square cm. (2½ tons per square inch) gives a result of about 100 hours.[3] In the latter case the oxides of nitrogen can diffuse away, but in the former they do not diffuse so fast as they are formed, and yet the blocks are sufficiently porous to allow oxygen to diffuse into them.

If air be quite excluded, the NO is further reduced to innocuous compounds, nitrogen suboxide (laughing gas, N_2O) and nitrogen. Thus it was found by Vieille [4] that after heating Poudre B for twenty days at 75° in an atmosphere of carbon dioxide, the residual gas after absorption of the carbon dioxide had the following composition :

CO	7
NO	13
N_2O	8
N_2	72

The composition of the gases that accumulated in submarine mines containing compressed gun-cotton, which had been hermetically closed and immersed in water for seven or eight years, was found to be :

[1] *J.C.S.*, 1907, vol. 91, p. 764. [2] Robertson, *Seventh Inter. Cong. Appl. Chem.*, 1909, vol. iii*b*, p. 95.
[3] *P. et S.*, vol. xv., 1910, p. 64. [4] *P. et S.*, vol. xv., p. 92.

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O_2 . . .	0·3	—	0·33
CO_2 . . .	2·1	2·3	2·09
CH_4 . . .	0·5	0·85	0·43
H_2 . . .	6·5	5·93	6·52
N_2O . . .	1·5	1·0	1·42
N_2	88·9	89·05	88·61
	99·8	99·13	99·40

The gases were collected over water.[1]

The fact that nitro-glycerine powders do not become porous, even when the solvent has all escaped, renders them less liable to attack by atmospheric oxygen. Poudre B, on the other hand, is somewhat porous even when new.

In the presence of water nitric peroxide forms nitric acid, which, as already stated, has a strong hydrolytic decomposing effect on nitro-cellulose and nitro-glycerine, especially the latter.[2] The explosives always contain several tenths per cent. of water which they have absorbed from the atmosphere; moreover, water is one of the normal products of the deterioration of the substances. The moisture plays an important part in the decompositions, and one of the greatest problems in devising satisfactory stability tests lies in the difficulty of regulating the amount of water present in the material which is undergoing the tests. In the entire absence of water, the oxides of nitrogen only assist the oxidation of the material; no hydrolysis can occur. On the other hand, if the amount of water present be very large, the acids are diluted so much that their action is much diminished. There is an intermediate amount of moisture which causes a maximum of decomposition. Nitric acid, although injurious, is liable to be destroyed by reacting with the nitro-cellulose; moreover, it is volatile and consequently may escape altogether. Sulphuric acid, on the other hand, is practically permanent, and so unless there be some basic substance present, which will neutralize it, it has a much worse effect. It is, no doubt, for this reason that the presence of sulphuric esters is so very injurious, for in course of time they lead to the formation of sulphuric acid. The organic acids, formed in the deterioration of the explosives, are so weak in their action that they are not very harmful.

The presence of foreign particles in explosives may diminish the stability, thus Thomas at the 5th International Congress of Applied Chemistry (Berlin, 1903) recorded a case in which the accidental imbedding of the head of an iron nail caused the spontaneous decomposition of a nitro-glycerine powder. Partly nitrated foreign matter, derived from impurities in the cotton used, has a deleterious effect too, as also have various other kinds of foreign matter. Therefore all extraneous bodies should be eliminated as far as practicable during manufacture.

[1] *Loc cit.*, p. 63.

[2] *See* Silberrad and Farmer, *J.C.S.*, vol. 89, 1906, p. 1759.

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Stabilizers. The idea of adding substances to these explosives to combine with the acid products of decomposition, and so prolong the life of the material, occurred at an early date. Von Lenk treated the gun-cotton with a solution of sodium silicate and then washed it. It was shown by Abel [1] that the beneficial action was due to the precipitation of calcium carbonate in the fibres by the interaction between the sodium silicate and the calcium salts in the water used. When gun-cotton is stabilized by boiling in hard water, calcium carbonate is similarly precipitated in it to the extent of several tenths per cent., and it has been found that this is necessary for the stability of the material, if it is to be stored for a considerable period of time. When very soft water is used, it has been found necessary, in some instances, to add carbonate.

Strong alkali in aqueous solution has a much greater hydrolytic action on nitro-cellulose than acid. Silberrad and Farmer found that caustic baryta acted 480 times as fast as nitric acid under the same conditions. Therefore only such alkaline substances should be employed as are practically insoluble in water. The carbonates of calcium and magnesium are those that are generally used ; to nitro-glycerine blasting explosives 1 or 2 per cent. of these substances are often added. Ammonium carbonate has also been used for this purpose ; it is such a weak base that it cannot have a very powerful hydrolytic action, in spite of its ready solubility in water, but it is objectionable on other grounds : it is volatile and deliquescent, and it dissociates into carbon dioxide and ammonia, which reacts with the nitric esters and accelerates their decomposition.

On storage the alkali gradually becomes neutralized, being converted mostly into nitrate, together with some nitrite, but a few tenths per cent. of calcium carbonate will enable a well-prepared gun-cotton to withstand even tropical temperatures for a great many years.

Although gun-cotton containing calcium carbonate is more stable than that containing none, it gives a lower heat test. This is apparently due to the fact that at the temperature of the test, the calcium nitrite present decomposes more readily than the gun-cotton, giving off oxide of nitrogen, which affects the test paper. By washing such a gun-cotton with distilled water, so as to remove soluble salts, the heat test is improved.

Ureas. Basic compounds, to neutralize the acids formed, are not the only substances that have been added to explosives to increase their stability. There are also various other substances, which can react with the oxides of nitrogen to form innocuous compounds. Urea has been used extensively as a stabilizer for celluloid,[2] and was at one time a constituent of American military powders. It reacts with nitrous acid to form carbon dioxide and nitrogen :

$$CO(NH_2)_2 + 2HNO_2 = 2N_2 + CO_2 + 3H_2O,$$

[1] *Phil. Trans. R.S.*, 1867, p. 181.

[2] *See* Worden, *Nitrocellulose Industry*, p. 596.

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but it also attacks the nitro-cellulose, and is no longer employed as an ingredient of explosives. By substituting organic radicles for the hydrogen atoms it is stated that the injurious action is prevented. J. Stevens found diethyl-diphenyl-urea, $CON_2(C_2H_5)_2(C_6H_5)_2$ and tetraphenyl-urea $CON_2(C_6H_5)_4$ the best.[1] It is stated that dimethyl-diphenyl-urea, called Centralite, is being tried in France as a surface gelatinizing agent.[2] The use of these compounds for this purpose has been patented by Claessen.

Amines.

Aniline $C_6H_5NH_2$ was formerly used in Italy as an addition to Filite. With nitric peroxide it forms diazo-benzene nitrate, which, however, is unstable and breaks down into phenol and nitric acid. By replacing another of the hydrogen atoms attached to the nitrogen more satisfactory stabilizers are produced.

The use of diphenylamine $(C_6H_5)_2NH$ as a stabilizer was patented by Nobel in 1889, and it has been used in Germany for this purpose for some twenty years. As there do not seem to have been any serious spontaneous ignitions of smokeless powder in that country, the fact is significant. Diphenyl-amine has also been adopted by Italy, Sweden, and Spain. In France it was under trial for many years, and since October 1910, it is added to all Poudre B.[3] In the United States 0·45 per cent. is incorporated with the nitro-cellulose smokeless powder,[4] and it is claimed officially that the life of the powder is thereby increased from six or seven years to twenty years or more.[5] Secondary and tertiary amines, such as di- and triphenyl-amine with nitrogen peroxide form nitrous-compounds, which are comparatively stable. There is, however, considerable field for research to ascertain which of the many available amine derivatives or other compounds are the best stabilizers.

From the results of a few heat tests carried out by Guttmann's method, Carneiro concluded that diphenyl-amine is injurious to the stability.[6] This difficult question cannot be settled so easily, however. It is only by keeping quantities for periods extending over several years, under conditions resembling the most severe that are likely to be met with in actual storage, combined with chemical investigations of the changes that take place, and stability tests at intervals of time, that definite conclusions can be reached, and even then the results must be interpreted with care. Such trials have been conducted in France and have given favourable results, and the same has presumably been the case in America also.

Mineral jelly.

Mineral jelly, which was originally added to cordite for quite other reasons,

[1] U.S. Pat. 593,787 of 1897 ; Russ. Pat. 12,649 of 1907.
[2] Florentin, *La Technique Moderne* ; *S.S.*, 1913, p. 32.
[3] Florentin, *La Technique Moderne* ; *S.S.*, 1913, p. 7.
[4] Worden, *Nitrocellulose Industry*, p. 907.
[5] Report *U.S. Joint Army and Navy Board, U.S. Naval Institute Proceedings*, March 1912.
[6] *S.S.*, 1909, p. 30.

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has been found to have a great stabilizing effect. It is a very complex mixture of hydrocarbons, many of which are unsaturated and are able to combine with the oxides of nitrogen. Also by forming an impervious layer on the outside of the sticks, it preserves the explosive from oxidation by the air.

Phenanthrene. Spica has proposed the addition of phenanthrene $C_{14}H_{10}$ to smokeless powders to improve the stability, and also to reduce the temperature of explosion.[1]

Amyl-alcohol. It was found in France that the presence of residual solvent in Poudre B added to its chemical as well as its ballistic stability. To some extent the increase in chemical stability is no doubt due to reaction of the alcohol with the oxides of nitrogen, with formation of nitrous and nitric ether, but its effect is apparently due principally to its preventing the powder becoming degelatinized and consequently more porous. The presence of solvent thus impedes the oxidation of the nitro-cotton. As ethyl-alcohol is inconveniently volatile, it was partly replaced by amyl-alcohol, which has a higher boiling-point.

Aromatic ethers, etc. Nathan, Rintoul, and Baker, in a series of patents (12,742 to 12,746 of 1912), have pointed out that it is necessary that a stabilizer be capable of being incorporated uniformly into the smokeless powder, and that it shall not separate out during the drying. They have found several different classes of substances which are suitable in this respect and react rapidly with the oxides of nitrogen: aromatic ethers, such as ethyl-naphthyl-ether $C_{10}H_7.O.C_2H_5$; derivatives of carbaminic acid, such as methyl-phenyl urethane; urea derivatives, such as ethyl-phenyl urea; and anilides and derivatives of other acid amides, acet-ortho-toluidide $CH_3.C_6H_4.CH_2.CO.NH_2$, for instance. Of any of these 5 per cent. may be introduced into cordite MD in the place of the mineral jelly.

[1] *S.S.*, 1912, p. 129.

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CHAPTER XXXV

STABILITY TESTS

Trace tests : Abel heat test : United States directions : Nitro-glycerine : Explosive gelatine : Gun-cotton : Smokeless powder : Precautions : Significance of heat test : Other trace tests : Fume tests : Vieille test : German 135° test : Waltham Abbey silvered vessel test : Quantitative tests : Will test : Bergmann and Junk test : Other quantitative tests : Light tests : Examination of stabilizer

In the early days of the manufacture of nitro-cellulose there were no methods known for readily distinguishing a stable from an unstable explosive, and the result was a series of devastating explosions which practically put a stop for a time to the new industry, and it was only after Sir Frederick Abel had introduced the " heat test " that it was possible to carry on the manufacture of modern explosives with safety. Although this test has many imperfections, and a large number of other tests have been proposed to replace it, it is still the one that is most used, as it is very simple and easy to carry out, and the other tests are also not free from faults.

Classes of tests.

Nearly all the stability tests that have been proposed depend on the detection or measurement of the nitrogen oxides given off when the explosive is heated to a more or less elevated temperature. The first class of these tests is that of the so-called " trace tests," in which the explosive is heated at a moderate temperature, such as 160° or 180° F. (70° or 80° C.), and the time taken to colour a very sensitive test-paper or solution is observed. The Abel test belongs to this class. The second division is that of the " fume tests," in which the sample is heated at a considerably higher temperature, 100° to 135°. and the time noted until it commences to fume, or until it affects some less sensitive reagent, such as litmus-paper. The third class, that of the " quantitative tests," comprises those in which the gun-cotton is heated at a fixed temperature within about the same limits as those of the " fume tests," and measurements are made of the amount of the oxides of nitrogen or the total products of decomposition given off in a fixed period of time.

The Abel Heat Test

In the Abel heat test a certain quantity of the explosive prepared in the prescribed manner is placed in a test-tube (Fig. 125). The test-tube is closed

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with a rubber stopper through which passes a glass rod terminating in a hook from which is suspended a piece of sensitized paper. This consists of filter paper impregnated with potassium iodide and starch, and the upper half is

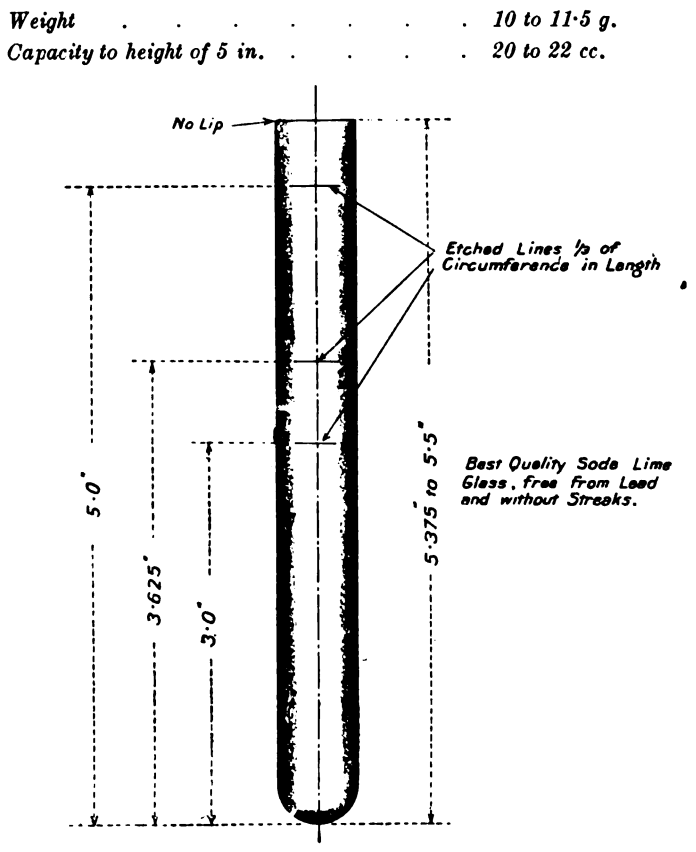

FIG. 125. Heat Test Tube

(From First Report of Heat Test Committee, by permission of the Controller of H.M. Stationery Office)

moistened with a mixture of equal volumes of glycerine and water. The lower part of the test-tube is then immersed in a water-bath kept at the prescribed temperature and the time is taken which elapses until a faint brown line appears on the paper at the dividing line between the wet and dry portions.

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As there was much uncertainty as to the exact way in which the test was to be carried out, and the procedure of the Home Office was different to that

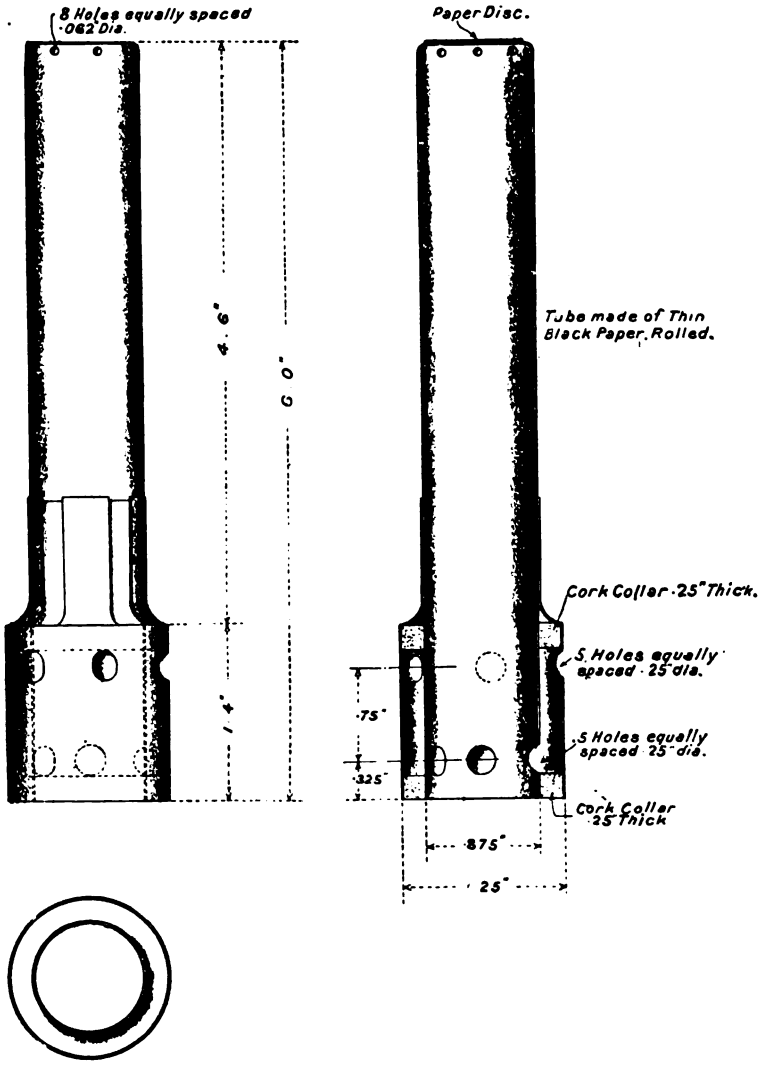

FIG. 126. Cap for Heat Test Tube
(From First Report of Heat Test Committee, by permission of the Controller of H.M. Stationery Office)

of the War Office, a joint Committee was appointed in April 1909, representing the Home Office, the Admiralty, the War Office, and the explosives trade, to make investigations with a view to obtaining greater uniformity in the methods

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and materials used, and also to consider alternative tests. This Committee presented its first report in February 1914, together with a Memorandum giving detailed instructions as to the methods to be employed and specifications of all the apparatus and materials employed.[1] This Memorandum should be consulted. As light shining on the test-paper was found to shorten the test, a black cap (Fig. 126) was introduced. The tube is kept covered with this until shortly before the end of the test. The following Table shows briefly the temperatures, quantities and times for different sorts of explosives :

Explosive			Temperature of heat test bath	Quantity of explosive heat tested	Time explosive should stand the test
Class	Division	Nature			
			°F.		min.
3	1	Nitro-glycerine extracted from dynamite, etc., by displacement with water	160 (71·1° C.)	2 c.c.	15
		Carbonite, Monobel and similar friable nitro-glycerine preparations from which the nitro-glycerine cannot conveniently be extracted by water	160 (71·1° C.)	3·2 grammes	7
		Blasting Gelatine, Gelatine Dynamite and analogous preparations	160 (71·1° C.)	3·2 ,, + 6·5 ,, French chalk	10
		Cordite,[1] Ballistite and other propellants of Class 3, Division 1	160 (71·1° C.)	1·6 grammes	10
3	2	Nitro-cellulose pulp, compressed Gun-cotton, Tonite and analogous compressed nitro-cellulose preparations	170 (76·7° C.)	1·3 grammes	10
		Nitro-cellulose propellants	170 (76·7° C.)	1·3 ,,	10
		Ammonite, Bellite, Roburite and analogous preparations	170 (76·7° C.)	1·3 ,,	10
[1] For the acceptance of new Cordite and Cordite M.D. supplied for his Majesty's Naval and Military Services, the details are fixed by the Admiralty and War Office as follows:					
		Cordite and Cordite M.D.	180 (82·2° C.)	1·6 grammes	30

United States Directions for the Heat Test

The regulations issued by the military and naval authorities of the United States differ considerably from the English ones. They are given in full. Blasting gelatine, gelatine dynamite, and analogous preparations are also submitted to liquefaction and exudation tests.

[1] *First Report of the Departmental Committee on the Heat Test as Applied to Explosives.* Wyman and Sons, 1914.

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The water-bath of the potassium-iodide-starch testing-apparatus is brought to 160° F. (71·1°), and maintained at that temperature, being regulated by the thermometer which should be immersed about 2¾ inches in the water. The source of heat should be carefully watched, and at no time should the temperature of the bath rise or fall more than 1° F. from 160° F. Fifty grains of nitro-glycerine are placed in each test-tube and carefully weighed, care being taken not to get any on the sides of the test-tube; this may be done by using a suitable dropper or glass tube.

A piece of test-paper is taken with the pincers and laid down on a piece of clean filter-paper. The test-paper is held in place by the end of a glass rod which has been thoroughly cleaned, heated, and cooled. A small hole is made in the test-paper with the point of the pincers opposite the middle of one end of the paper and about 0·2 inch from the edge. The test-paper is taken up with the pincers, the platinum hook inserted through the hole just made, the hook bent with the pincers until the throat of the hook is closed tightly on the paper so that it will stand stiffly up when the paper is held vertically above the glass rod. The glass rod with test-paper is placed carefully aside under a bell glass or other protecting cover where it will be protected from fumes and dust. In the same way the other test-papers are prepared.

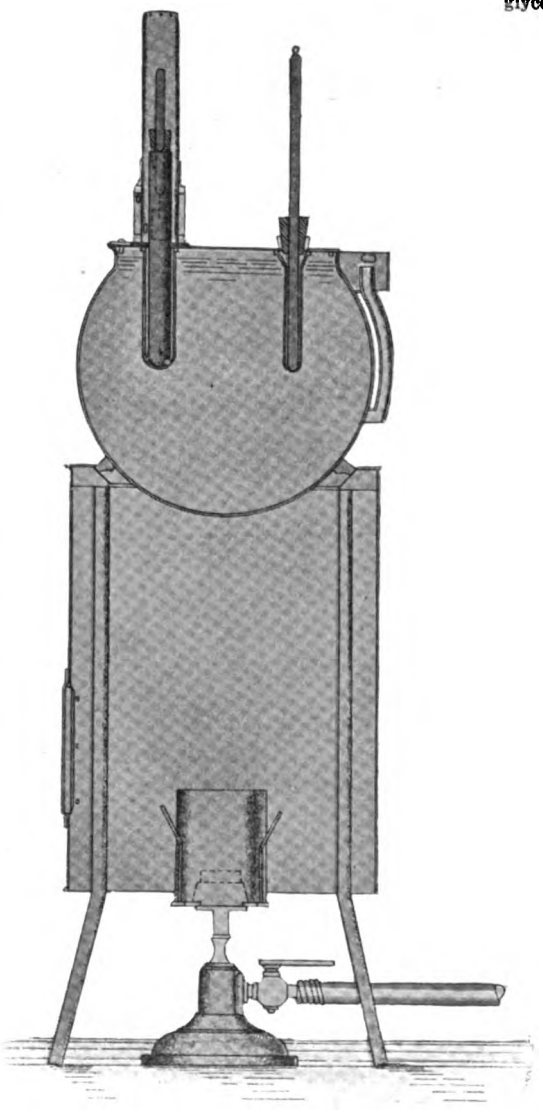

Fig. 127. Heat Test Bath Assembled
(From First Report of Heat Test Committee, by permission of the Controller of H.M. Stationery Office)

A solution of pure glycerine and distilled water, in equal volumes, is prepared.

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One of the test-papers is taken, held with the paper up, and a drop of the glycerine solution is placed on each of the lower corners of the test-paper, as held ; the paper should absorb this evenly about half-way to the opposite upper edge, leaving a distinct line about midway between the moistened and the unmoistened parts. One of the test-tubes is placed in the bath through one of the apertures in the cover and is immersed until the sample is below the surface of the water. The test-paper, moistened with glycerine, is placed in the test-tube, and the glass rod is moved through the cork until the line between the moistened and unmoistened parts of the test-paper is about $\frac{5}{8}$ of an inch above the upper surface of the cover. This time is recorded. The same is done with each of the other two test-papers. The line between the moistened and unmoistened parts of each test-paper is watched carefully, and the exact instant that a faint brown colour [1] appears on this line of demarcation on each test-paper is recorded. This completes the test.

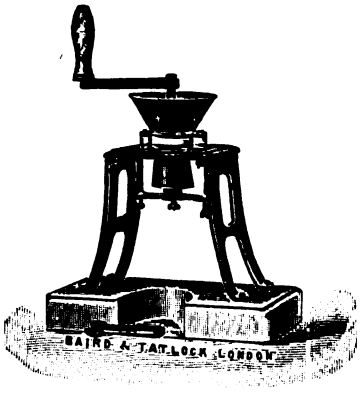

FIG. 128. Mill for Cordite

The nitro-glycerine under examination will not be considered " thoroughly purified " unless the time elapsed between the insertion of the test-paper and the appearance of the brown colour is at least fifteen minutes. The average of the records of all the tubes will be taken.

Explosive gelatine. If explosive gelatine is under examination a sample of 50 grains is intimately incorporated with 100 grains of French chalk, using a wooden pestle in a wooden mortar. The French chalk should be of good commercial quality, should be thoroughly washed with distilled water, dried in a water-oven, and then exposed to moist air under a bell jar until it has taken up about 0·5 per cent. of moisture. It should then be placed in a glass-stoppered jar for use.

Each test-tube is filled with this mixture to a depth of $1\frac{3}{4}$ inches, the tube being gently tapped on a table to insure a proper degree of settling.

The heat test is then conducted as explained for nitro-glycerine. Explosive gelatine will not be considered as serviceable unless the average time of the test is at least ten minutes.

Gun-cotton. The following are the tests for nitro-cotton as revised by the U.S. Ordnance Department, April 18, 1908 : [2] The sample is pressed in a clean cloth or wrung in a wringer, if it contains a large excess of water. The cake is rubbed up in a cloth until it is a fine powder, taking care that it does not come in contact

[1] In order to detect this colour promptly, the water-bath should be so placed that a bright reflected light falls on the papers.

[2] Worden, *Nitrocellulose Industry*, p. 969.

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with the hands. It is spread out on clean paper trays, and dried in an air-bath at 35° to 42°, just sufficient time to reduce the moisture to that amount which will give a minimum heat test, this amount being from 1½ to 2 per cent. If, as sometimes happens in dry weather, the moisture has been reduced to less than 1·5 per cent., the sample must be placed in a moist atmosphere for a time not exceeding two hours, until the required moisture is obtained. The whole time of drying and making the test must not exceed eight hours.

The sample thus prepared is weighed out into five test tubes, 1·3 g. (20 grains) in each tube, so that a series is obtained covering the widest variation allowed for moisture. These tubes are 5·5 inches long, ½ inch internal diameter, and ⅝ inch external diameter, closed by a clean cork stopper fitting tightly, through which passes a tight glass rod with platinum holder for the paper. The corks are discarded after one test. The nitro-cellulose is pressed or shaken down in the tube until it occupies a space in the tube of 1⅝ inches. The test paper, about 1 inch in length and 0·3 inch wide, is hung on the platinum holder, and moistened on its upper half with a 50 per cent. solution of pure glycerine in water. The heating bath, carefully regulated at 65·5° ± 1°, is placed so that a bright reflected light is obtained, the tubes are placed in the bath and the time is noted. As the test proceeds, a slight film of moisture condenses on the inside of the tubes, and the line of demarcation between wet and dry test paper is kept abreast of the lower edge of the moisture film. The first appearance of discoloration of the damp portion of the test-paper marks the end of the test for each separate tube, the minimum test of any one of the five tubes being the heat test of the nitro-cellulose. The standard water-bath is made long and narrow to reduce to a minimum the heating of the upper part of the tube.

Smokeless powder.

The sample should be prepared by cutting into slices 0·02 inch thick. These slices are exposed to the air for at least twelve hours.

The test-tube sample consists of 1·3 g.

The usual potassium iodide test is followed, except that the temperature is considerably higher for simple nitro-cellulose powders, being 100° (212° F.) instead of 65·5° (150° F.). Each sample must stand this temperature without showing a brown line for ten minutes.

Powders containing nitro-glycerine should stand the test at 65·5° for twenty minutes.

Precautions

It is of the utmost importance that all the operations connected with the Abel and other trace tests be conducted in a room that is quite free from acid fumes, as the test is affected by very minute traces of acids and other bodies. If heat tests have to be carried out frequently it is best to keep a special room for the purpose or, better still, a special building remote from any place where

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acid or other fumes are generated. The operator also must be careful not to introduce anything that can affect the test: he should wash his hands before starting the test and should not wear clothes that can have become contaminated.

In 1901, Cullen called attention to the desirability of having a uniform official source for the heat test-papers used throughout the British Empire,[1] as very trifling differences in the method of preparation affect the results considerably. Heat test-papers can now be obtained from official sources.

The United States Government also issue heat test-papers to the manufacturers who contract to supply it with explosives.

If heat test-papers from other than the official source be used, it is necessary to compare them with the official papers as regards sensitiveness by carrying out duplicate tests, or test them by the "diffusion test" described in the Memorandum on the Heat Test.

The objections to the test are due to its extreme sensitiveness. On the one hand, samples that are really stable sometimes give low heat tests, because they have become contaminated with minute traces of some material which is really harmless but affects the iodide and starch paper; ozone, for instance, has a powerful effect. On the other hand, samples of insufficient stability sometimes give high tests, because they contain traces of some substance that interferes with the reaction between the oxides of nitrogen and the paper. *Mercuric chloride* is a substance of this kind, for an extremely small proportion will lengthen the heat test of the sample very considerably. In Germany it has been usual to carry out the final washing of gun-cotton with water containing a little of this salt, ostensibly in order to prevent the growth of fungus on the gun-cotton; but this object can be better achieved by using phenol (carbolic acid), and it seems probable that the real object is to improve the heat test. At any rate, this is the view that has always been taken by the authorities in England, and they regard the addition of mercuric chloride or any similar masking agent as a most reprehensible practice. Tests for traces of mercury compounds are given elsewhere (p. 545).

There are many other substances, which mask the Abel heat test, and so make the explosives containing them appear much more stable than they really are. Ethyl acetate and alcohol prolong the test greatly, and consequently it cannot well be used to test powders gelatinized with them, at any rate, when they are new. Acetone, on the other hand, has little or no effect on the test. Dupré found that the carbonates of calcium and magnesium had no appreciable effect, whereas sodium carbonate prolonged the heat test of bad samples of explosives with which it was mixed, but decreased that of good ones.[2] Camphor, aniline, diphenyl-amine, mineral jelly, and many other substances, which react with the oxides of nitrogen, prolong the heat test,

[1] *J. Soc. Chem. Ind.*, 1901, vol. 20, p. 8.

[2] *A.R.*, 1887, p. 22.

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but in many cases this prolongation corresponds to a real improvement in the stability.

In old explosives the masking agents, if originally present, become exhausted, but varying quantities of a large number of decomposition products are present (*see* Chapter XIII, p. 170), which may affect the heat test, either lengthening or shortening it. Besides the organic compounds, water, nitric and nitrous acids are among the products, and as they are volatile, they may cause considerable fluctuations in the results, according as they are allowed to escape more or less before the test is applied. Oxalic acid shortens the heat test,[1] but probably does not affect the stability greatly.

Significance of heat test.

Robertson and Smart have carried a number of experiments and calculations to ascertain the significance of the results of the Abel heat test in the case of nitro-glycerine and ungelatinized gun-cotton.[2] They found that the quantity of nitric peroxide required to produce the standard tint on the service heat test paper is 135×10^{-6} mg., a figure which is very near that arrived at in the laboratory of the Düneberg Explosives Factory, namely, 4×10^{-5} mg. nitrogen, equivalent to 131×10^{-6} mg. NO_2.[3] When the papers are exposed to an unlimited quantity of air containing nitric peroxide, the time required to produce the standard tint is inversely proportional to the concentration of nitric peroxide: for the service papers the product of the time in minutes, by the concentration, in mg. of nitric peroxide per c.c., is 31×10^{-6}. From theoretical considerations Robertson and Smart deduced the equation:

$$T = \frac{KV}{Q} \log \frac{r}{r + \frac{Q^2}{KV^2} - \frac{QrT}{KV}}$$

where Q is the quantity of nitric peroxide required to produce the tint, 135×10^{-6}

K the product of the time into the concentration, 31×10^{-6}

V the unoccupied volume of the heat-test tube, 18 c.c.

r the rate of rise in the concentration of nitric peroxide in the heat test-tube due to decomposition of the explosive.

and T the time.

From the results obtained in the Will test and from other data it is calculated that for good gun-cotton $\log r = \cdot 06021\, t - 10 \cdot 6928$, where t is the temperature in °C. But there is a lag in the time of the test due to the fact that at first the gun-cotton is colder than the bath. The rate of rise of temperature was actually measured by means of a thermocouple. Taking into consideration the results thus obtained, the time for the heat test of gun-cotton was calculated for different temperatures and compared with those observed:

[1] Bravetta and Parrozzani, *Stabilité des Nitro-cellulosee*, 1908, p. 17.

[2] *J.S.C.I.*, 1910, p. 130. [3] *Mitt. aus der Centralstelle*, Heft 3, p. 28.

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Temp. °C.	r	Time from equation	Lag	Calculated time	Observed time
		hr. min.	min.	min.	min.
70	0·332	27	4	31	28, 29
72	0·43	21·5	4	25·5	25, 25½
74	0·59	17	4	21	21, 21½
76.7	0·84	13	4	17	15
79·5	1·24	10	4	14	12
82·25	1·81	7·5	4	11·5	11½
100	21·26	1·75	4½	6·25	4½

The agreement, taken in conjunction with the results of other experiments, shows that in the case of fibrous gun-cotton the Abel heat test represents the decomposition of the gun-cotton itself during the test, and is not due to dissolved impurities. But with gelatinized smokeless powders, that have been made some time, this is not the case; the gun-cotton dissolves considerable quantities of nitrogen peroxide, which are not entirely given up again by the comparatively compact material, even when it is exposed to the atmosphere for some days in the ground state.

The reason why it is necessary to regulate the quantity of moisture in the gun-cotton is that, when very dry, it gives a high test owing to the drying of the test paper, whereas very wet gun-cotton also gives a high test, because the excess of water condenses in the tube and absorbs much of the nitric peroxide.

Since the heat test of a gun-cotton is only a measure of its initial decomposition, the test cannot be regarded as an absolute indication of its stability. In the Will test non-volatile catalysers may not give rise to a high rate of decomposition until fifteen or thirty minutes have elapsed at a temperature of 135° C., and this at 170° F. (76·7° C.) would correspond to a period of some days.

When nitro-glycerine is heat tested in the ordinary way, the result obtained is very much higher than would be expected from the known rate of its decomposition, which is more than nine times as rapid as that of gun-cotton

$$\log r = \cdot 06021\ t - 9\cdot 7312.$$

This is due to the fact that the nitrogen peroxide formed mostly remains dissolved in the liquid, from which it can only escape slowly because but a very small surface is exposed. The result is largely dependent on the amount of oxide of nitrogen that has accumulated in the liquid. If a large surface be exposed by mixing the nitro-glycerine with silica wool, the results obtained agree with those calculated.

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When small quantities of gun-cotton are added to nitro-glycerine, the heat test rises, owing either to the oxide of nitrogen being more soluble in the gun-cotton, or to the increased viscosity of the liquid. When sufficient gun-cotton has been added to break up the surface of the liquid, the heat test falls rapidly, but on account of the felting of the fibres the comminution is never so perfect as when silica wool is used. If the gun-cotton contain sulphuric ester, it greatly accelerates the decomposition of the nitro-glycerine, and low heat tests are obtained. In the following experiments the gun-cotton A contained 0·15 per cent. of alkaline matter expressed as calcium carbonate, B was neutral, and C contained 0·7 per cent. of sulphuric acid as sulphuric acid ester :

Per cent. N/G	Per cent. G/C	Temperature of test	Type of gun-cotton used		
			A	B	C
			min.	min.	min.
100	0	180°	19	14½	19
0	100	170°	17	17	16
97·5	2·5	180°	31	—	21
95	5	180°	32	15	30
90	10	180°	86	38	34
80	20	180°	28	13	9
70	30	180°	17	—	6
60	40	180°	13	6½	4

Other Trace Tests

Zinc iodide and starch test.

In Germany, the Netherlands, and some other countries a modification of the Abel test is used in which zinc iodide is substituted for potassium iodide, and it is claimed that the test is thereby rendered more sensitive. This, however, is hardly an advantage, as the principal fault of the Abel test is its excessive sensitiveness. In Spain a paper is used impregnated with a solution containing starch, zinc iodide, and zinc chloride.

Guttmann's test.

Guttmann carried out a series of experiments to find a reagent which would not be masked by solvents such as ether-alcohol and ethyl-acetate, nor by such substances as mercuric chloride.[1] He decided upon a paper impregnated with diphenylamine in sulphuric acid solution. Of the diphenylamine 0·100 grm. is dissolved in 40 c.c. of water together with 10 c.c. of concentrated sulphuric acid, and when cold an equal volume of pure glycerine is added. Filter-paper is well washed, dried, and cut into strips 1·0 inch by 0·4 inch.

[1] *J.S.C.I.*, 1897, vol. 16, p. 293.

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One of these strips is suspended from a hook, as in the Abel heat test, and the top edge is moistened with two drops of the reagent, so that they run together and cover about a quarter of the paper. Otherwise the test is carried out like the Abel test at a temperature of 70°. The moistened part of the paper after a time becomes greenish-yellow and then a dark blue mark appears at the dividing line between the moist and dry parts of the paper. This is the end of the test. The test has been adopted by the Belgian military engineers and is in use in several other countries, but unfavourable reports have been made by several investigators who have been unable to obtain concordant results with this test.[1]

Spica's test. In Spica's test m-phenylene-diamine hydrochloride and cane-sugar are used to impregnate the paper. This reagent is much more sensitive than potassium iodide and starch, and for this reason has not been adopted extensively.

Several other "trace tests" have been proposed, but none of them has come into general use. J. Moir, for instance, has suggested the use of Ilosvay's reagent, mixed with glycerine, which is so sensitive that the test can be carried out at 45°; or a dilute solution of indole in 50 per cent. glycerine.[2]

Egerton proposes to do away with the paper and expose the reagent on a piece of glass in a tube of special design.[3] He also uses Ilosvay's reagent, which he prepares by mixing together 5 c.c. of a 0·1 per cent. solution of α-naphthylamine containing a little acetic acid, 5 c.c. of a 0·5 per cent. solution of sulphanilic acid also containing a little acetic acid, and 10 c.c. of glacial acetic acid.

Fume Tests

Vieille test. In the Vieille test the explosive is heated at 110° in a closed tube with litmus-paper in a specially designed bath. The quantity of explosive taken is 10 g., preferably in one piece; this is heated in the bath for a day of eight hours or until the litmus-paper has assumed a standard red tint. Next day this is done again with a fresh piece of litmus-paper, and the procedure is repeated until the litmus-paper is reddened in one hour. All the times are then added together and the total time is noted. This test has been adopted officially in France and is also used considerably in other countries, but it is considered by some investigators to be unreliable.[4] Thus, in the Report on the *Jéna* Disaster[5] a case is mentioned in which duplicate tests on the same sample taken at different establishments gave results of twenty-two minutes and nineteen hours respectively, and at the same establishment duplicate tests

[1] *See also* Kullgren, *S.S.*, 1912, p. 153.
[2] *Eighth Inter. Cong. Appl. Chem.*, 1912, vol. iv., p. 81.
[3] *J.S.C.I.*, 1913, p. 331; also *J.S.C.I.*, 1914, p. 113.
[4] *See* Sy, *Jour. Franklin Institute*, 1908, vol. 166, pp. 249, 321, 433.
[5] Vol. iii., p. 130.

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often give very divergent results.[1] Sy ascribes the discrepancies to the difficulty in closing the tubes uniformly tightly.

German 135° test.

The German test at 135° C. is much used for nitro-celluloses. The following are the particulars of the method as carried out in the United States Ordnance Laboratory.[2] 2·5 grm. of the sample to be tested are dried at the ordinary temperature of the laboratory for twelve hours and placed in a strong test-tube. A piece of blue litmus is placed in the tube about ½ inch above the sample, the paper being folded lightly so as to give the folds sufficient elastic power to hold the paper in place by pressure against the sides of the tube. The tube is lightly closed by a cork with a hole 0·15 inch diameter bored through it, and so placed in a bath of boiling xylol (the boiling-point of which is 135°) that only 6 or 7 mm. project above the surface. Examination of each tube is made each five minutes after twenty minutes have elapsed. In making this examination the tube should be withdrawn only half its length and quickly replaced. Two tubes are used in each test, and there must be no failure in either tube. Three observations are made: (1) Time of *complete* reddening of litmus-paper; (2) time of appearance of brown nitric oxide fumes; (3) time at which the sample exploded.

Stable explosives should give the following times:

Explosive	Litmus not reddened in	No nitric fumes in	No explosion in
	hr. min.	hr. min.	hr.
Uncolloided nitro-cellulose . . .	0 30	0 45	5
Nitro-cellulose powders . . .	1 15	2 0	5
Nitro-glycerine powders . . .	0 30	0 45	5

The results should be compared with that of a known stable explosive of the same kind, under the same test by the same operator, using the same test paper. Ungelatinized nitro-cellulose should be well shaken down in the tube by tapping, or lightly pressed down.

Waltham Abbey silvered vessel test.

The Waltham Abbey silvered vessel test is one which has been adopted by the War Office for the examination of Cordite Mark I, which has been in the Service for some time and gives a low heat test. It has been designed to imitate the conditions of storage as closely as possible; it is applied if the heat test at 160° F. is below eight minutes and above four minutes. Full instructions for carrying out the test are given in the *Regulations for Army Ordnance Services*, Part II (Wyman and Sons, 1908), pp. 162 to 167. The cordite is ground as for the heat test and about 50 g.

[1] Vol. iii., pp. 177, 215.

[2] *See* Sy, *J. Franklin Inst.*, as above, *also J. Amer. Chem. Soc.*, 1903, vol. 25, p. 550.

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are placed in a glass vessel surrounded with a vacuum jacket silvered to reduce loss of heat. To the neck of the vessel and at right angles to it is fused a long tube, which permits the observation of any red fumes as soon as they are given off. A thermometer is introduced through the neck into the centre of the powder. These vessels are placed in recesses in the top of a bath, which is maintained at such a temperature that the thermometers indicate 80° ± 0·1°. After a time red fumes will appear in the side tube, and a few hours later the temperature of the cordite begins to rise. The time is noted when the temperature has risen 2·0°. A good cordite when new will stand this test for 500 or 600 hours. When the test has fallen below a certain limit the cordite is considered " unserviceable " and is destroyed. The test should be carried out in a special building in consequence of the danger of explosion of the considerable quantities of cordite involved. The temperature of the bath is kept constant by using a Lowry regulator if a gas supply be available; if not, the bath must be provided with a reflux condenser and filled with a liquid which boils at the right temperature; a mixture of water and methylated spirit is suitable.

Quantitative Tests

Will test. In the Will test, which is used as a rule only for ungelatinized nitro-cotton, the explosive is heated at a temperature of 135° in a current of dry carbon dioxide, and the nitrogen evolved is measured every quarter of an hour; 2·5 g. of the dry nitro-cotton are weighed out into the tube z, into which the carbon dioxide passes through a spiral tube fused on to its lower end.[1] The rate of flow of the gas is rendered apparent by bubbling it through sulphuric acid, which at the same time dries it. Will generated the carbon dioxide in a Kipp's apparatus from marble and hydrochloric acid, using special precautions to free it from air, but Robertson prefers to take it from cylinders of the compressed gas carefully selected. In either case the gas must be tested, and a correction introduced for the air it contains. From the tube z (Fig. 129) the gases pass to a copper tube *U*, containing metallic copper and copper oxide, which is maintained at a red heat. This destroys all organic gases, converting the carbon and hydrogen into carbon dioxide and water; nitrogen compounds are converted into elementary nitrogen. Hence the gases are led to the measuring tube *G*: this is filled with strong caustic soda solution of specific gravity 1·2; at its lower end there is a zig-zag to facilitate the absorption of the carbon dioxide. Carbon dioxide is passed through the apparatus until all air has been displaced, then the oil-bath *B*, which is kept at 135°, is raised and the test starts. There is a stirrer in the bath worked

[1] *See Mitteilungen aus der Centralstelle*, Heft 2, 1900; Heft 3, 1902; *also* Robertson, *J.S.C.I.*, 1902, p. 819.

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by a water-motor or other convenient means, and the whole is enclosed in the cupboard *S*, which keeps off draughts and protects the operator in the event of an explosion. Robertson has modified the apparatus in some details; he passes the gas at the rate of 1000 c.c. per hour instead of 1500, the rate used by Will, as he finds that the slower rate shows up bad gun-cottons more effectively.

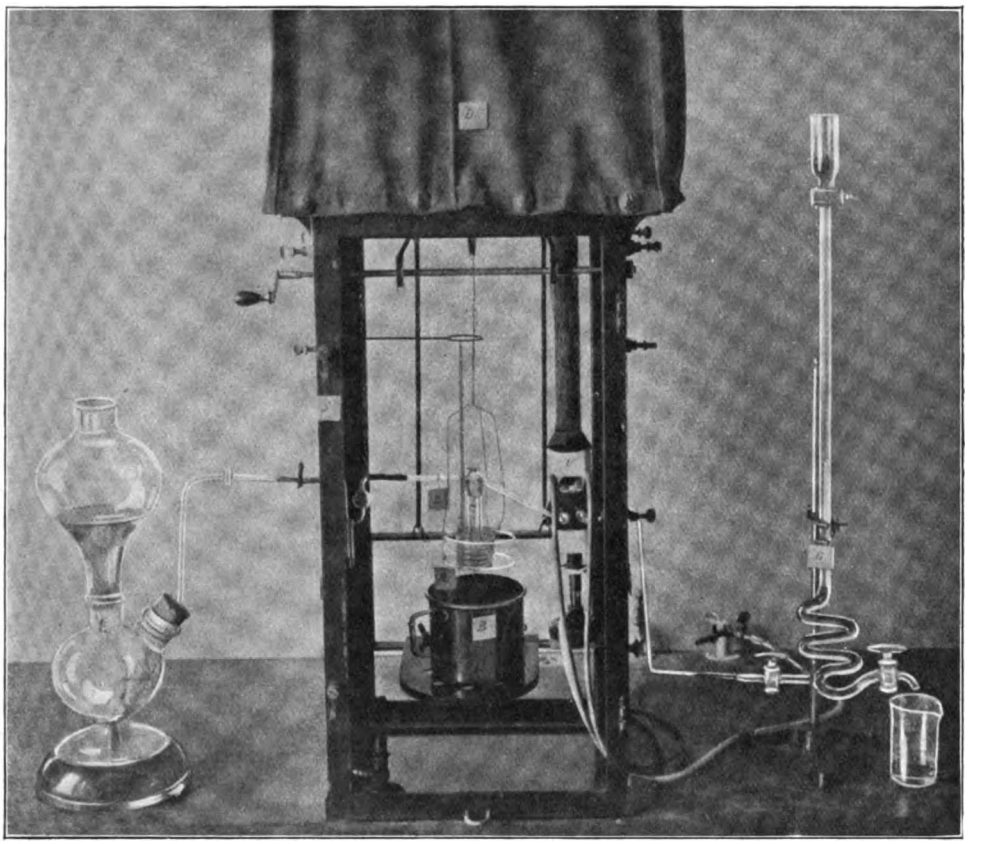

FIG. 129. Will's Test for the Stability of Nitro-cellulose

The results given by the test are reliable, provided care be exercised to ensure that the apparatus is air-tight and working properly in all respects. A good gun-cotton evolves nitrogen at a uniform rate; for Service gun-cotton containing about 13 per cent. of nitrogen Robertson found that the quantity evolved in four hours by 2·5 gr. was from 6·5 to 8·5 mg. Nitro-cottons less highly nitrated decompose less rapidly, provided they have been stabilized equally well. One reason why the Will test gives such uniform and satisfactory results is, no doubt, that air and moisture are excluded.

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Robertson and Napper [1] have carried out experiments with a number of modifications of the test, and have thereby thrown considerable light on the composition of the gaseous products of decomposition, and their reciprocal influence on the decomposition.

Bergmann and Junk test.

The Prussian military authorities and the German Railway Commission have adopted a test devised by Bergmann and Junk.[2] It has the merit of being quantitative and does not require such an elaborate apparatus as the Will test. In this test the gun-cotton is heated in a glass tube at 132°, and the nitrous gases are absorbed in water, and when the heating is finished they are estimated by the Schultze-Tiemann method. The glass tube has thick walls and is 35 cm. long and 2 cm. in internal diameter. Into the neck is

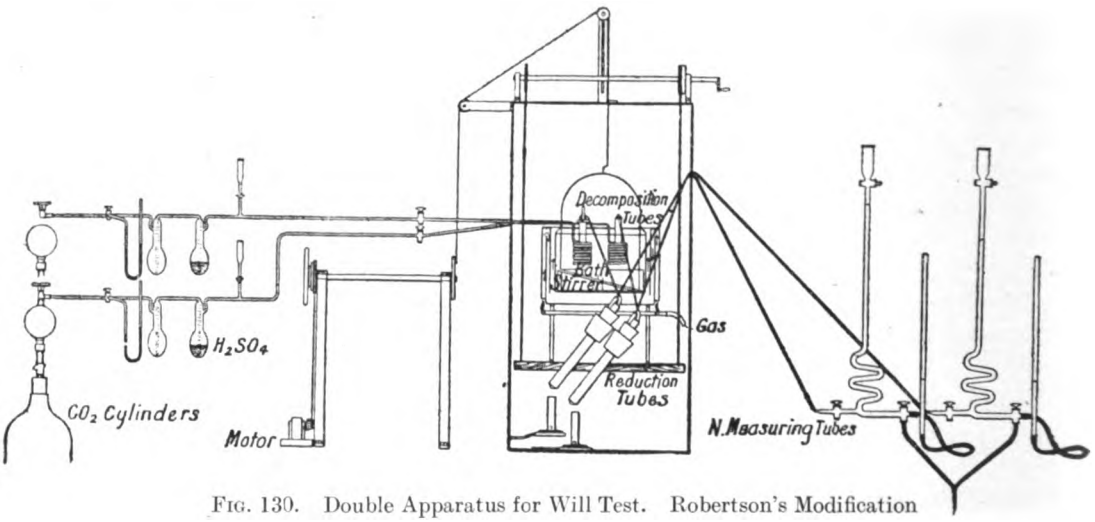

FIG. 130. Double Apparatus for Will Test. Robertson's Modification

ground a hollow glass stopper, which is surmounted by the absorption apparatus shown, *D* or *E*, Fig. 132.

The heating bath is a rectangular copper vessel 35 cm. × 10 cm. × 25 cm. high, with ten tubes, each 20 cm. long, let into it to take the glass tubes. It is also fitted with a reflux condenser and a small tube to take a thermometer; it is filled with amyl-alcohol, which is kept boiling by means of a burner.

In the authors' paper there is a description of an elaborate wooden cupboard to take the testing apparatus, so that in case of an explosion the effects may be confined. It is, however, expensive and greatly increases the danger of fire. A large piece of plate glass should be erected in front of the apparatus with a piece of woven wire of coarse mesh before it, and there should be an arrangement of cords and pulleys to enable the operator to remove any tube from the bath without handling it.

[1] *J.C.S.*, 1907, T., p. 761.

[2] *Ang.*, 1904, p. 982.

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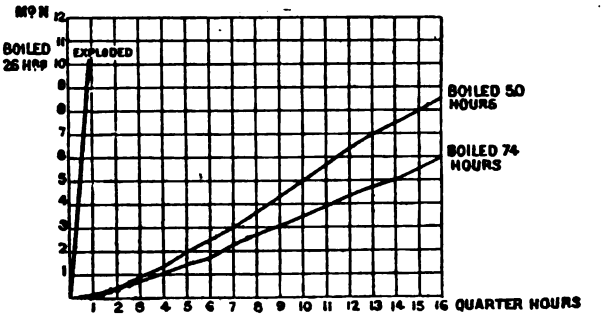
The gun-cotton is dried in a bath with a good current of air at a temperature of 40° to 50° for three hours. Then it is passed through a sieve of 2 mm. mesh, and the drying is continued in a vacuum desiccator over sulphuric acid until it contains not more than 1 per cent. of water; 2 g. are weighed out and introduced into the tube, any particles adhering to the sides being removed by knocking the tube or brushing it down with a feather. The glass stopper is slightly lubricated with good mineral lubricating oil and is inserted, the absorption apparatus is half-filled with water, and the glass tube is introduced into one of the holes in the bath, which should be at a temperature of 132°. The heating is continued for two hours or other convenient time, and then the tube is removed from the bath. As the air in the tube contracts the water is drawn out of the beaker *g* on to the cotton. If the bulb apparatus *E* be used, it is necessary to add some water at the end of the test to cause it to siphon over into the tube. The absorption apparatus is washed out into the tube, and the volume is made up to the 50 c.c. mark, which is on the tube. The liquid is then filtered through a dry filter, 25 c.c. of the filtrate are taken, 1 c.c. of N/2 potassium permanganate solution is added to oxidize the nitrous to nitric acid, and the nitrogen is estimated by the Schultze-Tiemann method. A good gun-cotton in two hours should not give more than 2·5 c.c. of nitric oxide.[1] Dupré came to the following conclusion concerning the test:



Service gun-cotton. Influence of boiling

FIG. 131. Results of Will Tests

"It was found, in the first place, that duplicate experiments with the same sample of gun-cotton gave as a rule very concordant results, but that, in the second place, the test was influenced to a considerable degree by variation in the percentage of moisture in the samples tested. This was more especially found to be the case when the sample was not perfectly purified, and might thus easily lead to mistaken decisions with regard to the rejection or approval of samples near the limit of purity, unless certain limits of moisture are very rigidly observed.

"The test is scarcely influenced at all by the presence of perchloride of mercury, which, as is well known, renders our heat test inapplicable, but like this latter test it is greatly influenced by the presence of urea. The test is also greatly affected by the condition of the gun-cotton tested, *i.e.* whether gelatinized or simply pulped, the former giving far lower results than the latter. The test in its present form is not applicable to nitro-glycerine prepara-

[1] *A.R.*, 1904, p. 28. *See also A.R.*, 1905, p. 28.

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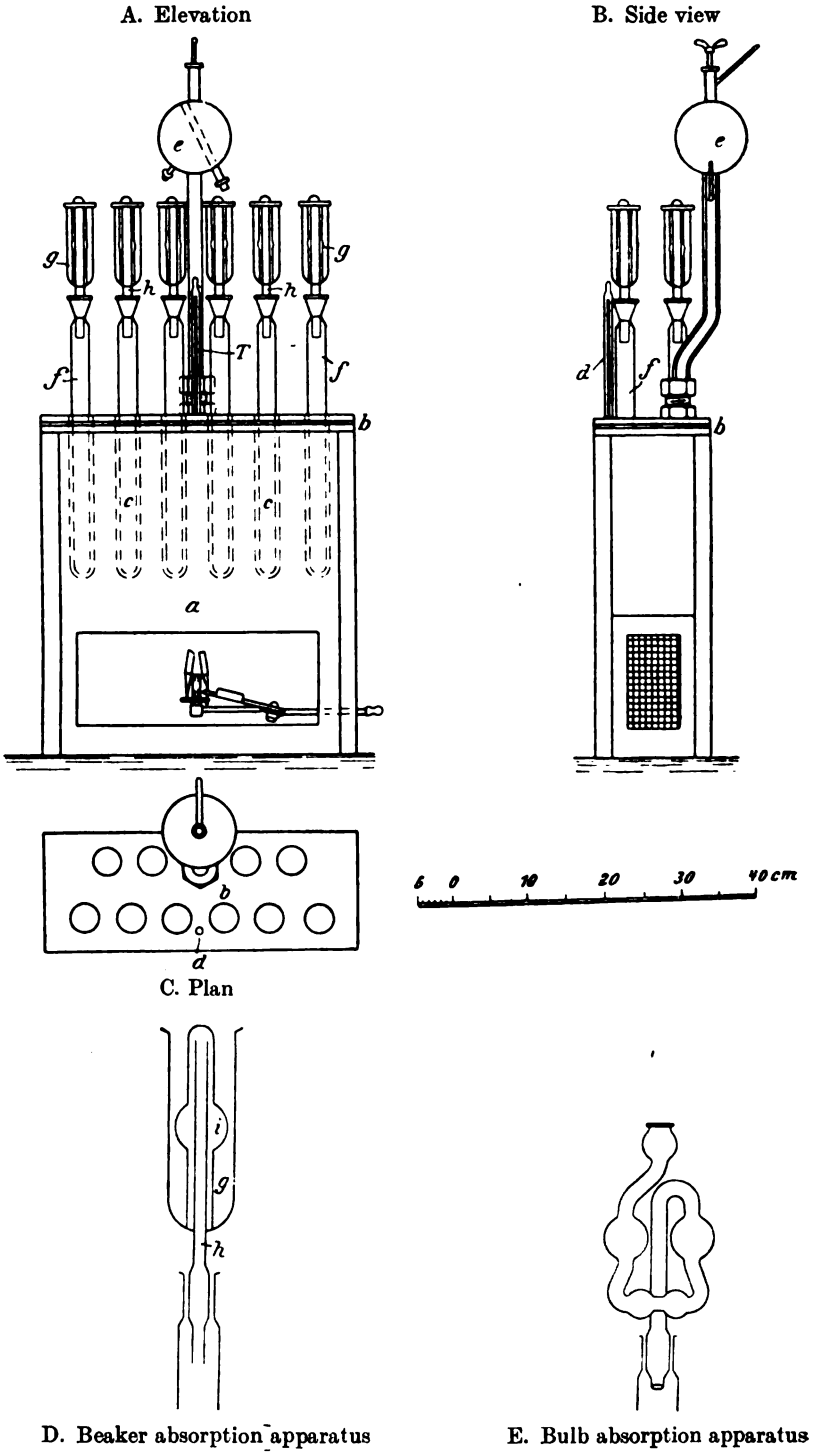

FIG. 132. Bergmann and Junk Stability Test for Nitro-cellulose

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tions or to such as contain nitrates, and does not distinguish so sharply as the heat test between the various stages of washing of gun-cotton. Lastly, in spite of all care taken, tests made on the same sample gave occasionally widely different results, due perhaps to the fact that the products of decomposition are left in contact with the sample throughout the test, whereby very small differences in the rate of decomposition at the beginning of the experiment would be greatly aggravated at the end."

Other quantitative tests.

Various investigators have devised tests in which the gun-cotton is heated *in vacuo* to a temperature of 130° to 150°, and the evolution of gas is measured, generally by means of a manometer. Obermüller described a test of this kind,[1] and Willcox has given the results of determinations with it on American gun-cottons :[2] Pleus has given details of apparatus for carrying it out.[3] Dupré has used a similar method and reported favourably on it.[4] Brame also has devised a test of this sort.[5] Robertson and Napper have pointed out the necessity of preventing moisture depositing in the tubes leading away from the decomposition vessel.[6] The method gives results as satisfactory as those of the Will test, if proper precautions be taken.

Mittasch heated gun-cotton at the ordinary pressure at 150° and recorded the increase of volume automatically.[7] Silberrad devised a similar test, in which the gun-cotton was dried and then heated at 115° for twenty hours, and the gas evolved was measured over water.[8] Dupré found that duplicate tests with the same sample conducted side by side occasionally gave widely different results.[9]

Silberrad[10] has also proposed a test for smokeless powders, in which the unground powder is heated at a temperature of 70° in a limited quantity of air, and the rate and duration of the gas evolution, or contraction due to absorption of the oxygen, is observed. The results do not seem to bear any relationship to the real stability of the powder.

Light Tests

Abel in his classical Researches on Gun-cotton[11] investigated the action of sunlight on this explosive. He found that it became acid and evolved gases much more rapidly than in the dark. When thoroughly stabilized the decomposition was less rapid than when part of the stabilization process was omitted. If the gun-cotton was wet, the decomposition was considerably greater than

[1] *Berlin Bezirksverein der Verein deutscher Chemiker*, October 11, 1904 ; *J.S.C.I.*, 1905, p. 347.
[2] *J. Am. C.S.*, vol. 30, p. 271 ; *S.S.*, 1908, p. 247.
[3] *S.S.*, 1910, p. 121.
[4] *A.R.*, 1903, p. 26 ; 1904, p. 28 ; 1905, p. 29.
[5] *J.S.C.I.*, 1912, p. 161.
[6] *J.C.S.*, 1907, T., p. 764.
[7] *Ang.*, 1903, p. 929 ; *see also* Saposhnikof, *P. et S.*, vol. 14, p. 42.
[8] *Treatise on Service Explosives*, 1907, p. 141.
[9] *A.R.*, 1905, p. 28.
[10] *Ibid.*
[11] *Phil. Trans. R.S.*, 1867, 181.

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if it was air-dry, which is the reverse of what is found when the gun-cotton is stored in the dark. Abel ascribed this phenomenon to oxidation of the gun-cotton at the expense of the water under the influence of the light. It took months or years to obtain a marked evolution of gas from a stable gun-cotton; for this reason, and because of the variability of sunlight, but few attempts have been made to investigate the stability of explosives by insolation. Berthelot and Gaudechon have carried out a number of experiments, in which various explosives have been enclosed in quartz tubes and exposed to ultra-violet light from a mercury lamp.[1] They find that the gas evolved from Poudre B in good condition consists of carbon monoxide and dioxide and nitrogen, whereas from deteriorated powder nitrous and nitric oxides are also given off. Nitro-glycerine and nitro-glycerine powders give off the oxides of nitrogen even when new, and hence the authors conclude that nitro-cellulose powders have a greater intrinsic stability than those that contain nitro-glycerine. A test which submits an explosive to conditions fundamentally different from those it will have to undergo in actual use, cannot, however, fairly be used to compare substances of different types, though possibly it may afford evidence of the comparative stability of explosives of the same sort.

Examination of Stabilizer

Although many of the above tests give fairly satisfactory results when used for the examination of freshly manufactured explosives, when they are applied to old explosives, such as smokeless powders which have been stored in a hot climate for some years, great difficulties are encountered. The products of deterioration accumulated in the powders affect the results, and at high temperatures they may bring about decomposition of quite a different kind from that which occurs at the ordinary temperature of storage. On the other hand, it is often practically impossible to prevent the escape of a considerable proportion of the volatile products of decomposition during the preparation of the sample and the course of the test. If a stabilizing agent was originally added to the explosive, useful information can often be obtained by examining it. In the case of compressed gun-cotton, for instance, into which a small proportion of calcium carbonate was incorporated during manufacture, the course of the deterioration can be ascertained by determining how much of it has been converted into nitrite and nitrate, and how much is still unchanged. And from the results the probable future life of the gun-cotton can be calculated.

If the explosive contain diphenylamine, the gradual exhaustion of the stabilizer can be followed by means of the colour reactions that it gives. Nitroso-diphenylamine is first formed, which is pale yellow in colour. Accord-

[1] *C.R.*, 1911, p. 1220; 1912, pp. 201 and 514.

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ing to Berger [1] the maximum quantity of nitrosamine is present in the powder when one-half to two-thirds of its life has been run. Further action of the nitrogen oxides on the nitrosamine converts it into dinitro- and then trinitro-compounds, the latter appearing when eight or nine tenths of the life of the powder is past. Florentin states that the dinitro-product gives a characteristic red coloration with alcoholic caustic soda solution; the trinitro-derivatives give the same reaction, but also colour red an alcoholic solution of potassium cyanide.[2]

[1] *Bul. Soc. Chim.*, 1912, p. 1.
[2] *La Technique Moderne*; *S.S.*, 1913, p. 8.

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PART XI

MATERIALS AND THEIR ANALYSIS

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MATERIALS AND THEIR ANALYSIS

Acetone : Acids, Sulphuric, Nitric, Mixed, Waste acid : Antimony sulphide (stibnite) : Azides, Sodium, Lead azide : Chlorhydrin, Dichlorhydrin, Chlornitro-hydrin, Dichlornitro-hydrin : Cotton, Absorption of dye, Copper value, Wood-gum, Alkali oxide copper : Diphenylamine : Ether : Fulminate of mercury, Manufacture, Properties, Estimation : Fulminate of silver : Glycerine : Glycerine nitrates (lower) : Dinitro-glycerine, Mononitro-glycerine : Graphite : Hexanitro-diphenylamine : Kieselguhr (guhr, infusorial earth) : Mercury, Detection of traces by spectroscopic methods, Microscopic methods : Mineral jelly (petroleum jelly, vaseline) : Moisture (volatile matter) : Nitrates, Saltpetre, Sodium nitrate, Ammonium nitrate : Nitro-benzenes, Mono-, Di-, Trinitro-benzene : Nitro-cellulose, Properties, Nitrogen Detection, Estimation, Determination of nitrogen, Solubility, Matter insoluble in acetone, Unnitrated fibre, Free acid and alkali, Discoloration, Ash, Microscopic examination, Sulphuric esters, Viscosity of solutions, Fineness : Nitro-glycerine, Properties, Physiological action, Detection, Examination, Estimation : Nitro-toluenes, Dinitro-toluene, Trinitro-toluene : Picric acid, Manufacture, Properties, Dangers, Detection and estimation, Examination, Density : Picrates and trinitrocresylates, Ammonium picrate : Sulphur : Tetranitraniline : Tetranitro-methyl-aniline : Wood-meal

ACETONE

$CH_3.CO.CH_3$

(*See also* Chapter XXI)

THE specific gravity should not be more than 0·800 at 15° compared with water at the same temperature. It should be colourless and miscible with water in all proportions without turbidity, and should leave practically no residue on evaporation.

Permanganate Test. A 100 c.c. graduated flask is filled up to the mark with the acetone at a temperature of 15°, and 1 c.c. of a 0·1 per cent. solution of potassium permanganate is added, and the two are mixed. The characteristic colour of the permanganate should persist for at least thirty minutes. This test is affected by light, and should be carried out in the dark or in a dim light. It excludes various organic impurities.

The deterioration of acetone is greatly accelerated if it contain acids or certain amines. These are tested for by diluting with an equal volume of distilled water and adding a few drops of a saturated solution of para-nitrophenol or other suitable indicator. It should be quite neutral to this indi-

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cator, or only show very slight alkalinity. No acid should be present except carbonic, which is determined by diluting with boiled distilled water and titrating with standard caustic alkali, using phenolphthalein as indicator. The amount of carbon dioxide should not exceed 0·002 per cent.

In Germany acetone is tested for neutrality with phenolphthalein which, when added to 10 c.c. of the acetone, must not be reddened, but the addition of 1 c.c. N/10 alkali must cause a red coloration. It is also specified that it shall not contain more than 0·1 per cent. of "aldehyde," which is tested for with a solution made by dissolving 3 g. silver nitrate, 3 g. caustic soda, and 20 g. liquid ammonia (specific gravity 0·9) in water and making up to 100 c.c.: 10 c.c. of the acetone are mixed with 10 c.c. distilled water and 2 c.c. of the silver solution, and left covered in the dark for a quarter of an hour. The liquid is then poured off from the reduced silver, and tested with a pale dilute solution of ammonium nitrate to see whether excess of silver be still present. If there be, it is supposed that the amount of aldehyde in the acetone is less than 0·1 per cent. Although acetones occasionally fail to pass this test, it is doubtful whether the failure is ever due to aldehyde, the quantity of which seldom exceeds 0·01 per cent. There is no method of determining accurately small quantities of aldehyde in the presence of large quantities of acetone, but they can be estimated approximately by colorimetric tests with Schiff's reagent, a solution of magenta decolorized with sulphurous acid. If 2 c.c. of acetone be dissolved in 100 c.c. of water and 1 c.c. of the reagent be added, the liquid gradually assumes a purple colour, which is distinctly stronger if 0·01 per cent. of aldehyde has previously been added to the acetone.

The test with ammoniacal silver nitrate solution is really a test for the light oils which are present in acetone and are insoluble in water. These can be determined by actual measurement as follows: 100 c.c. of the acetone are mixed with 200 c.c. of water in a retort, and rapidly distilled. The first 10 c.c. of distillate is collected in a graduated cylinder, 20 c.c. of water are added, and if the liquid becomes cloudy, the cylinder is stoppered and allowed to stand. The volume of oil that separates at the top of the liquid is then read off, if there be sufficient to give a reading. A cloudiness of the liquid in the cylinder indicates that the quantity of the impurity in the acetone is not less than 0·02 per cent.

A more convenient test for the same impurity is carried out with N/10 iodine solution (12·69 g. iodine and 14·60 g. potassium iodide dissolved in 1 litre water): 100 c.c. of water at a temperature of 15° are placed in a beaker, 10 c.c. of the acetone are then run in and mixed with the water, and then 2 c.c. of the iodine solution. Exactly one minute later the same quantity of N/10 thiosulphate solution is run in, and the excess is then titrated with N/100 iodine solution; 1 c.c. of this is equivalent to about 0·02 per cent. of

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the impurity. If the quantity required be more than 10 c.c., the test should be repeated, using larger quantities of N/10 iodine and thiosulphate. Provided there be a sufficient excess of iodine, the results are not affected by the quantity of it added. They are also not affected by light, and only slightly by variations in the proportion of water and acetone used, or by small differences in the time of action, or by such quantities of alkaline bodies as are liable to be present in a good acetone. The temperature should be regulated carefully.

Acetone can be estimated by Messinger's method: 2 g. of acetone are weighed out and dissolved in 500 c.c. water; of this solution 10 c.c. are measured out, mixed with 25 c.c. N/1 alkali, and 50 c.c. N/10 iodine solution are added. The liquid is shaken frequently for fifteen or twenty minutes, then 26 c.c. of N/1 sulphuric acid are added, and the iodine is titrated with N/10 thiosulphate solution. The test depends upon the conversion of the acetone into iodoform, whereby 6 atoms of iodine are absorbed for each molecule of acetone. In Germany it is required that the acetone shall show at least 98 per cent. by this test.

Acetone can also be estimated by the method of Jolles,[1] which depends upon the fact that a molecule of acetone combines with a molecule of sodium bisulphite to form a compound, which no longer reacts with iodine in neutral solution. The standard bisulphite solution is added to the acetone solution in a quantity three or four times as great as the theoretical amount, and the excess is titrated with standard iodine solution, after the mixture has been allowed to stand for not less than thirty hours. A blank determination should be made simultaneously.

ACIDS

Sulphuric Acid. The specific gravity is usually determined, but in the case of C.O.V. gives but little indication of the exact strength, which is generally ascertained by titration. It may, however, be estimated by diluting to about 75 per cent. strength with a known proportion of water and determining the specific gravity.[2] The mineral matter is determined by evaporating in a platinum basin and igniting (*see also* Chapter VII).

Nitric Acid. The specific gravity in this case affords a measure of the strength, when corrected for nitrous acid (*see* Chapter VIII), which is determined by dissolving 5 g. in a litre of water and titrating with N/10 permanganate solution until the colour remains for at least fifteen minutes; 1 c.c. is equivalent to 0·00235 g. HNO_2. The residue is determined by evaporation on a water-bath, and is tested for sulphuric acid. The nitric acid is also tested for chlorides.

Mixed Acid. The total acidity is determined by titration, the nitric and nitrous acids together by means of the nitrometer, and the nitrous acid by

[1] *Ber*, 1906, p. 1306.

[2] Marshall, *J.S.C.I.*, 1902, p. 1511.

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titration with permanganate. The percentages of nitric and sulphuric acid are then obtained by subtraction. The sum of the nitric and nitrous acids can also be estimated by precipitation with nitron. Direct determination of the sulphuric acid by evaporating off the nitric acid on a water-bath and subsequent titration gives low results ; precipitation with barium chloride is also unreliable.[1]

Waste Acid from the nitration of cellulose can be analysed by the same methods. That from the manufacture of nitro-glycerine presents difficulties, because a few per cent. of nitro-glycerine dissolve in the acid with partial decomposition. In the nitrometer the nitro-glycerine gives off the whole of its nitrogen ; it is better therefore to use nitron.

ANTIMONY SULPHIDE

(STIBNITE)

Sb_2S_3

This material is found native in England and other countries ; it is refined by fusion, and then forms bluish-grey lumps with a metallic lustre and very brittle. It is also produced artificially, but in Germany it is forbidden to use the artificial product, or such as contains iron. It is absolutely essential that it should be free from sulphuric acid, as this has a very deleterious effect on the stability of explosive mixtures containing a sulphide and a chlorate, such as cap compositions. When treated with *aqua regia* it should not leave a residue of more than 0·5 per cent.

For the determination of antimony sulphide in cap composition Brownsdon [2] has given the following method : After determining the fulminate by titration, the insoluble residue, containing the antimony sulphide and other substances, is filtered off on a small filter-paper, which is well washed and then transferred to a large test-tube. Five c.c. of strong hydrochloric acid are added and the contents of the tube boiled gently for a few seconds until the sulphide is dissolved and all the sulphuretted hydrogen has been driven off or decomposed. Three c.c. of a saturated solution of tartaric acid are then added and the contents of the tube washed into a conical flask of about 250 c.c. capacity. The solution is then nearly neutralized with sodium carbonate, excess of bicarbonate is added, and after the introduction of some starch solution the liquid is titrated with N/20 iodine solution. This method for small quantities of stibnite is both quick and accurate : the error does not exceed 0·0003 g.

[1] Lunge and Berl, *Ang.*, 1905, p. 1681.

[2] *J.S.C.I.*, 1905, p. 381.

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AZIDES

(TRINITRIDES)

These are the salts of hydrazoic acid (azoimide), N_3H, which has about the same strength as acetic acid, but in many of its reactions resembles hydrochloric acid.

Sodium azide, NaN_3, can be made by first leading ammonia gas over metallic sodium, whereby sodamide is formed, and then leading nitrogen suboxide over the product at a temperature of 150° to 250° : [1]

$$2NaNH_2 + N_2O = N_3Na + NaOH + NH_3$$

It forms clear colourless hexagonal crystals, optically uniaxial and strongly doubly refracting. One hundred parts of water dissolve 41·7 parts at 17° ; 100 parts alcohol 0·315 parts at 16° ; it is insoluble in ether. It has a slightly alkaline reaction and a very acid taste. It is not exploded by blows, and by heat only at a very high temperature. It is neither volatile nor hygroscopic, and is not decomposed by evaporation of its aqueous solution.

Lead azide, N_6Pb, is made by precipitating a solution of sodium azide with one of lead acetate. It is practically insoluble in cold water ; a litre of hot water dissolves about 0·5 g. When such a solution cools, crystals are deposited which are very similar to those of lead chloride ; these may be as much as a centimetre long, but such large crystals are extremely sensitive and have caused serious accidents. In a fine state of division the substance is comparatively safe, and is used for the manufacture of detonators (*see* Chapter XXIX).

CHLORHYDRIN

(CHLORPROPYLENE GLYCOL) $C_3H_7ClO_2$

$CH_2Cl.CH(OH).CH_2(OH)$

This substance may be made by heating glycerine with dry hydrogen chloride at a moderate temperature or with aqueous hydrochloric acid at a higher one. The reaction is assisted by the presence of acetic or other organic acid,[2] or of an ester, such as acetin.[3]

The product is heated *in vacuo* at about 70° to drive off the water and hydrochloric acid, then the temperature may be raised, and fractional distillation carried out *in vacuo*. A small quantity of dichlorhydrin distils over

[1] Wislicenus, *B.*, vol. 25, p. 2084.

[2] Böhringer and Söhne, Ger. Pats. 197,308 of November 20, 1906, and 197,309 of December 15, 1906.

[3] *Chem. Fabr. Griesheim-Elektron*, Ger. Pat. 238,341 of March 18, 1908.

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first, then monochlorhydrin, and finally unchanged glycerine. It is necessary to get rid of all the hydrochloric acid before raising the temperature, otherwise polymerization will take place. If the material is to be used for the production of low-freezing explosives, it is not necessary to submit it to fractional distillation, as the mixture of chlorhydrins and glycerine can be nitrated directly.

It may also be made by the action of chloride of sulphur on glycerine $2C_3H_8O_3 + 4SCl = 2C_3H_7ClO_2 + 2HCl + SO_2 + 3S$.[1] The sulphur can be made to separate out below by heating to 120°.[2]

Chlorhydrin has a specific gravity of 1·338 at 0°. Under atmospheric pressure it boils at 213° with some decomposition; under 18 mm. pressure it boils at 139°. It mixes in all proportions with water, alcohol and ether.

Dichlorhydrin

(DICHLORISOPROPYL ALCOHOL) $C_3H_6Cl_2O$.

$CH_2Cl.CH(OH).CH_2Cl$

This is made in the same way as the mono-derivative, only more hydrochloric acid or sulphur chloride is used and the treatment is continued longer. The statements as to its boiling-point and specific gravity are somewhat divergent, probably in consequence of impurities in some of the preparations. The mean value for the boiling-point is 176° to 177°. Under 10 mm. pressure it boils at 70°, and under 24·3 at 83° (Kahlbaum). The specific gravity is given as 1·383 at 0° and 1·367 at 19° by Markofnikof. It is soluble in 9 parts of water at 19° and 6 parts at 72°.

Chlor-dinitro-hydrin

(DINITRO-CHLORHYDRIN) $C_3H_5Cl(NO_3)_2$.

$CH_2Cl.CH(NO_3).CH_2(NO_3)$.

This is made from chlorhydrin by nitration with mixed acid in exactly the same way as nitro-glycerine is manufactured from glycerine. According to Roewer [3] it is a yellowish liquid of slightly aromatic smell, soluble in ether, alcohol, acetone, chloroform and other organic solvents, but insoluble in water and acids. It mixes with nitro-glycerine in all proportions. Specific gravity 1·54 at 15°. When heated it begins to give off red fumes at 180°. It boils with slight decomposition at 190° to 193° at atmospheric pressure. Under 15 mm. pressure it boils at 121° to 123°, giving an almost colourless distillate. It is very insensitive to blows and could not be exploded by the 2 kg. falling

[1] Carius, A., 122, 73; *Deutsche Sprengstoff A.-G.*, Ger. Pat., 201,230 of January 11, 1906.
[2] Ger. Pat. 229,872 of January 30, 1910. [3] *S.S.*, 1906, p. 229.

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weight even with a fall of 2 metres, nor yet by a 20 kg. weight. It is also insensitive to friction, but is readily detonated by fulminate. Roewer stated that the substance could not be made to freeze, but Kast [1] found that it solidified at a low temperature and melted again at temperatures varying from 1·5° to 6·8°; the divergence of these temperatures was probably due to the fact that the preparations did not consist of a simple substance, but of a mixture of different nitro-chlorhydrins.

Dichlornitro-hydrin or Nitro-dichlorhydrin, $C_3H_5Cl_2(NO_3)$ or $CH_2Cl.CH(NO_3)$. CH_2Cl may be made in the same way from dichlorhydrin. Its use in explosives has been protected by the Westfalisch-Anhaltische Sprengstoff A.-G.[2] It is described as a colourless liquid of specific gravity 1·459 at 15°.

COTTON

(*See* Chapter XI)

Whether the cotton be in the form of waste, cop bottoms, linters or any other, it should be as free as possible from foreign matter, such as string, seed particles or pieces of metal. The moisture is determined by drying in a water-oven; it should not be more than 7 or 8 per cent. The oily matter is determined by extracting in a Soxhlet apparatus with ether; formerly as much as 1 per cent. was allowed to be present, but now the amount is generally restricted to 0·4 per cent. or less. To ensure that the cotton has not been over-bleached and is reasonably free from oxy-cellulose and other reducing substances the "copper value" should be determined: this depends to some extent on the exact procedure in carrying out the test, but a standard method has been worked out by Schwalbe. A determination of the "alkali oxide copper" will show whether or not the cotton has been mercerized. The loss on boiling with caustic alkali under specified conditions may also be ascertained, or the "wood-gum" may be determined, but the insistence on low results by these tests may cause the supplier to submit the cotton to drastic treatment with caustic soda, whereby the cotton is really damaged.

Absorption of dye.

A measure of the amount of oxy-cellulose can also be effected by ascertaining the power to unite with basic dye-stuffs, such as fuchsine or methylene blue. Either the cotton may be treated with a dilute solution of the dye and well washed and the coloration compared with that taken by a standard sample under the same conditions, or the actual quantity of dye removed from solution may be ascertained. Lunge and Bebie [3] soaked 0·5 g. of the cotton in 150 c.c. of a 0·5 per cent. solution of methylene blue for an hour in a covered beaker standing on a boiling water-bath. When cold 100 c.c. were

[1] *S.S.*, 1906, p. 227.
[2] Ger. Pat. 197,404 of March 4, 1905.
[3] *Ang.*, 1901, p. 510.

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poured off and the colour was compared with that of the original solution by means of a colorimeter; 1 g. of pure cellulose took up 0·0012 g.

Copper value. Schwalbe's method for the determination of the copper value of cotton [1] is as follows: 3 g. air-dry cotton are cut into small pieces and mixed with 200 c.c. water and 100 c.c. Fehling's solution. The liquid is boiled for fifteen minutes under a reflux condenser with frequent agitation, the time being taken from the moment when full ebullition sets in. The liquid is filtered hot with the aid of a pump, and the residue containing cuprous oxide is washed with boiling water. The copper oxide is then dissolved in nitric acid and the amount of copper determined, preferably by the electrolytic method. The "copper value" is the percentage of metallic copper calculated on the dry cotton. The following are the results obtained with various materials:

	Copper Values	
Surgical cotton wool	1·64	1·8
Mercerized bleached Egyptian cotton yarn	1·9	1·6
Artificial silk (Glanzstoff)	1·1	—
Hydro-cellulose	5·2	5·8
Parchment paper	4·2	—
Bleached sulphite wood-pulp	3·9	3·9
Imitation ("greaseproof") parchment paper	3·5	3·0
Overbleached sulphite wood-pulp	19·3	—
Oxy-cellulose from filter paper and bleaching powder	7·7	7·6
Bleached cotton rag-pulp (half-stuff)	6·5	5·6

Wood-gum. Wood-gum is the substance, which is obtained by treating a cellulose with a solution of caustic soda and precipitating with hydrochloric acid. Fifteen g. of the dry cellulose are mixed with caustic-soda solution of exactly 5 per cent. strength, which is allowed to act for twenty-four hours with constant shaking at a temperature of 18° to 20°. The liquid is then pumped off and mixed with 100 c.c. of alcohol of 92·5 per cent. by weight and a little phenolphthalein; 9·5 c.c. of concentrated hydrochloric acid (specific gravity 1·19) are added, and normal acid is run in until the colour is just destroyed, and then a further 5 c.c. of normal acid is added. The liquid is allowed to stand twenty-four hours, then the precipitate is collected on a filter, which has been dried at 100° and weighed; it is washed with alcohol (92·5 per cent.) and then with ether, and dried at 100°.[2]

Wood-gum comprises the pentosans present in the material and also any oxy-cellulose formed by bleaching.

Alkali oxide copper. Alkali oxide copper is determined by Piest [3] by treating 3 g. of the cellulose for half an hour with 100 c.c. of Fehling's solution. It is then filtered off in a Gooch crucible, washed with boiling water, removed to a basin, and stirred

[1] *Ber.*, 1907, p. 1347; *J.S.C.I.*, 1907, p. 548.

[2] Kast, *Spreng- und Zündstoffe*, p. 919. *Ang.*, 1912, p. 2519.

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with 200 c.c. of boiling water. Twenty c.c. of a 0·5 per cent. solution of acetic acid are then added, the liquid is heated for a quarter of an hour and filtered ; the cotton is washed, and the filtrate is evaporated down to 300 c.c. ; 10 c.c. of 5 per cent. nitric acid are added and 2 c.c. of 10 per cent. sulphuric, and the copper present is determined by electrolysis. A normal cotton gives about 0·5 per cent. ; a mercerized cotton gave 1·47 per cent.

DIPHENYLAMINE

$(C_6H_5)_2NH$

This is a colourless crystalline substance melting at 54° and boiling at 310° ; it is insoluble in water, but readily soluble in alcohol and ether. It is only a feeble base, and its salts are decomposed with separation of the base. Its solution in concentrated sulphuric acid gives with a trace of nitrous acid an intense blue coloration. It is added to smokeless powder as a stabilizer (*see* Chapters XXXIV, XXXV).

It may be determined by saponifying the powder with strong caustic-soda solution, until its structure is destroyed, and then distilling with steam, until the distillate no longer gives a coloration with sulphuric acid containing a little nitric acid. The distillate is then shaken out with ether and the ethereal solution is dried with calcium chloride and evaporated. The residue is dried over sulphuric acid and weighed. If camphor or other volatile non-basic substance be present, the diphenylamine may be precipitated from the ethereal solution with dry chlorine gas, the precipitate filtered off in a Gooch crucible, washed with ether, dried for thirty minutes at 65° and weighed. Multiplication by the factor 0·83 gives the free diphenylamine.[1]

Dreger determines it as tetrabrom-diphenylamine.[2] The ethereal solution obtained as above is warmed with alcohol until the ether has been driven off ; then bromine is added drop by drop until there is an excess. The liquid is diluted with twice its volume of water and boiled until the alcohol and bromine have been driven off and the volume has been reduced to half. The precipitate of tetrabrom-diphenylamine is filtered off, washed with warm water and dried at 98° to 100° until the weight is constant. Multiplication by the factor 0·3487 gives the weight of diphenylamine.

[1] Kast, *Spreng- und Zündstoffe*, p. 958.
[2] *S.S.*, 1909, p. 123.

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ETHER

(ETHYL ETHER)

$(C_2H_5)_2O$

Pure ether has a specific gravity of 0·720 at 15° and boils at about 34·4° under 760 mm. It tends to take up a little moisture from the air, however, whereby the density is slightly increased, but the boiling-point is only slightly affected.[1] If it contain a little alcohol it can dissolve more water. If exposed to light and air, peroxides are liable to be formed, and these have an injurious effect on the stability of nitro-cellulose gelatinized with the solvent. They are tested for by shaking 10 c.c. of the ether with 1 c.c. of 10 per cent. potassium iodide solution in a completely filled glass-stoppered bottle; neither the ether nor the potassium iodide solution should be perceptibly coloured after standing for an hour in the dark.

Methylated ether is made from methylated spirit by the action of strong sulphuric acid. In addition to some alcohol and a little water, it contains dimethyl and methyl-ethyl-ether, which have greater solvent power for nitro-cotton, but boil at considerably lower temperatures than ethyl ether. The specific gravity of methylated ether varies from 0·72 to 0·73 or higher, the variation being principally due to the amount of alcohol and water in it.

FULMINATE OF MERCURY

$Hg(CNO)_2$

(*See also* Chapter XXIX)

Manufacture. Mercury is cleaned by squeezing it through wash-leather, 0·5 kg. is weighed out into a glass flask and 5·5 kg. of nitric acid (specific gravity 1·36) are added. When all the mercury has dissolved, the solution is allowed to cool, and then is poured into a large glass flask containing 5 kg. of alcohol of 90 per cent. strength, which has been warmed previously, if necessary, to a temperature of 20° or 25°. A reaction sets in almost at once accompanied by effervescence and the temperature of the liquid rises rapidly to about 80°; then the reaction moderates, but the temperature goes on rising slowly to 83.° Crystals of fulminate are seen to form, and the upper part of the flask is filled with white fumes. After about ten minutes red fumes appear, the evolution of gas becomes much more rapid, and the solid is formed faster; the temperature rises to about 86°, but its height depends to some extent on the outside temperature and other circumstances. Then the reaction moderates, and the fumes

[1] *See* Marshall, *J.C.S.*, 1906, Trans., p. 1384.

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in the reaction vessel become paler again. The total time of reaction is twenty to twenty-five minutes. The contents of the flask are then poured into water and washed by decantation until practically all the acid has been removed. In different factories the proportions of acid and spirit to mercury are varied somewhat,[1] but it is essential that a large excess both of nitric acid and alcohol be used, otherwise the yield of fulminate is much reduced; if only 6·5 parts of 60 per cent. spirit be used to 1 part of mercury, no yield at all is obtained. The yield is generally 1·2 to 1·3 of fulminate from 1 of mercury, whereas according to theory there should be 1·42.

The fumes given off in the reaction should be drawn off by means of a good draught, because if they condense in the reaction vessel, they have a deleterious effect on the product. They are conveyed into stone-ware bottles or tubes, where they are condensed as far as possible; they are very poisonous and inflammable. The condensate, which consists of ethyl nitrate and nitrite, aldehyde, unaltered alcohol, etc., is in some factories utilized to mix with fresh quantities of alcohol.

Pure fulminate is white, but the product obtained as just described is grey in colour or, if methylated spirit has been used instead of "commercial alcohol," brown, the coloration being due to traces of resinous substances formed in the reaction. If 1 part of metallic copper and the same quantity of hydrochloric acid be added to the nitric-acid solution just before it is poured into the alcohol, "white" fulminate is obtained, but analysis shows that this contains more instead of less impurity than the grey fulminate. The whiteness is apparently due to bleaching of the coloured bodies, and not to their destruction.

After the fulminate has been washed by decantation, it is collected on a muslin filter, and the washing is continued with distilled water until acidity can no longer be detected with litmus-paper. In some works it is washed with alcohol of 82 to 85 per cent. strength.

Properties.

To the naked eye fulminate looks like fine sand; under the microscope it is seen to consist of crystals of rhombic outline generally 0·01 to 0·1 mm. long. The specific gravity is 4·42 or 4·39.[2] A litre of water dissolves 0·7 g. at 13°, 1·7 at 49°,[3] and about 8 g. at 100°.[4] From water it is said to crystallize with half a molecule of water [5] in small fibrous crystals. Mercury fulminate dissolves readily in an aqueous solution of potassium cyanide, from which it can be reprecipitated with strong acid; pyridine also dissolves it easily and it can be recovered from the solution again by pouring into water. Philip, however, found that the best method for purifying small quantities in the

[1] *See* Solonina, *S.S.*, 1910, p. 42.
[2] Berthelot and Vieille, *Ann. Chim. Phys.* (5), vol. 21, p. 509; Solonina.
[3] Hollemann, *Rec. Trav. Chi.*, 1896, p. 159.
[4] Solonina, *S.S.*, 1910, p. 68.
[5] Schischkoff, *Lieb. An.*, 97, p. 54.

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laboratory is to dissolve it in ammonia, filter rapidly, and neutralize with 30 per cent. acetic acid.[1] Fulminate is also soluble in solutions of thiosulphate, especially if acid be added, but it is decomposed thereby. Concentrated hydrochloric acid also dissolves it with decomposition.

The residue left when the substance is dissolved in any of these solvents should be small, and when examined under the microscope, this residue should be free from particles of metallic mercury. The fulminate should be free from oxalates and chlorides.

Estimation. Brownsdon pointed out that when fulminate is treated with a solution of sodium thiosulphate, it dissolves with formation of alkali, and the fulminate can be determined by titration with standard acid,[2] which has been standardized on purified fulminate. This reaction has been investigated by Philip.[3] The results are in agreement with the equation :

$$Hg(CNO)_2 + 2Na_2S_2O_3 + 2H_2O = HgS_4O_6 + C_2N_2 + 4NaOH$$

but whether cyanogen is actually the product formed has not been established. Unless a large excess of thiosulphate be added, the alkalinity decreases again, so that low results are obtained in the titration ; but potassium iodide may be used instead to restrain this by-reaction, and to dissolve the fulminate. If the fulminate be dissolved with excess of the iodide and a known volume of standard thiosulphate, the excess of thiosulphate can also be titrated with standard iodine solution after the alkali has been neutralized with standard acid, and so a double estimation is effected on the same quantity of material. To this Philip has given the name of the " Bofors method " ; it is carried out as follows :

Fifty c.c. of N/10 thiosulphate solution is pipetted into a beaker, and about 3 g. of pure potassium iodide are dissolved in it ; 0·3 g. of the fulminate is rapidly washed in and the liquid is agitated until it is dissolved. The fulminate may be moistened beforehand with alcohol to prevent particles floating on the surface or forming lumps. A few drops of methyl-orange solution are now added and the solution is titrated with N/10 sulphuric acid ; then a little starch solution is added and it is titrated with N/10 iodine solution. The whole operation can be carried out in six minutes. The solutions may be standardized either by the ordinary methods, or upon fulminate of mercury that has been purified by means of ammonia and acetic acid, as above. One c.c. N/10 thiosulphate is equivalent to 0·01423 g. mercury fulminate, and 1 c.c. N/10 acid to 0·007115 gr. As a rule the fulminate shows the same percentage in both titrations, but in abnormal samples the acidimetric titration sometimes gives a higher result. A good grey fulminate will show 98

[1] *S.S.*, 1912, p. 223.
[2] *J.S.C.I.*, 1905, p. 381.
[3] *S.S.*, 1912, pp. 109, 156, 180, 198, and 221.

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to 99·5 per cent. of the pure substance; white fulminate generally gives results slightly lower, and fulminate purified with ammonia and acetic acid shows 100 per cent. within the limits of experimental error.

On keeping, fulminate is gradually converted into non-explosive compounds. The unaltered fulminate in a composition can be estimated by the above method, as the decomposition products do not react with the thiosulphate. The quantity of fulminate originally added to the mixture can be ascertained by determining the mercury by one of the usual methods.

FULMINATE OF SILVER

AgCNO

This is made in much the same way as fulminate of mercury, but as it is far more sensitive, it is only prepared in very small quantities at a time. It is too sensitive for use as an igniter or detonator, but it is employed in the manafacture of toy fire-works, such as bonbon snaps, throwdowns and crack shots. A thousand of these must not contain more than 15 grains of fulminate of silver.

GLYCERINE

(GLYCEROL)

$CH_2OH.CHOH.CH_2OH$

For the analysis of crude glycerine, standard methods have been adopted by an International Committee, which published a report in January 1911.

The glycerine used for the manufacture of nitro-glycerine is all distilled (*see* Chapter XV). The pure substance is colourless and has a specific gravity of 1·265 at 15·5° compared with water at the same temperature. Dynamite glycerine usually has a pale amber colour, and the specific gravity should not be less than 1·261. When diluted with 2 volumes of water, the solution should be clear; with litmus it should give no decided red or blue coloration; it should be practically free from sugars, fatty acids, salts of heavy metals and other impurities. Sugars and other carbonizable substances are tested for by adding to the glycerine in a test-tube an equal volume of concentrated sulphuric acid and allowing to stand for an hour; there should be no decided darkening of colour. Sugars may also be tested for by heating 5 g. with 50 c.c. water and a few drops of hydrochloric acid on a water-bath for half an hour, rendering alkaline with caustic soda and adding Fehling's solution: no yellowish-red cloud or precipitate should appear. Heavy metals are detected by adding sulphuretted hydrogen water; calcium, with ammonia and ammonium oxalate solution; sulphates, with barium chloride; oxalates, with calcium

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chloride; and chlorides, with silver nitrate solution. If, in the last test, the solution blackens, it indicates the presence of reducing substances; the test is made more delicate by the addition of a little ammonia. In none of these tests should there be indications of more than traces of the impurities. Organic impurities may be estimated by evaporating down at a temperature of about 160° and drying at the same temperature; there should not be more than 0·25 per cent. The ash left on ignition should not exceed 0·1 per cent.

A nitration test is sometimes carried out on a small quantity in the laboratory,[1] but the results thus obtained may be quite different from those yielded by the same glycerine on the manufacturing scale. It is therefore better to try a sample drum in the nitro-glycerine factory.

The following are the results of analysis of some representative samples of dynamite glycerine:

	per cent.	per cent.	per cent.
Salt	0·003	0·001	0·001
Ash	0·0032	0·001	0·002
Carbonaceous residue	0·04	0·012	0·018
Free acid	0·0042	0·0058	—
Combined acid	0·045	0·025	0·022
Specific gravity at 15°	1·2641	1·2632	1·2642

GLYCERINE NITRATES (LOWER)

Mono- and dinitro-glycerine were investigated by Will.[2]

Dinitro-glycerine may be made by adding 10 parts of glycerine to 33 parts of nitric acid (specific gravity 1·5) and then pouring on to a minimum of ice. The greater part of the product separates as an oily layer, but is mixed with some trinitro-glycerine. The yield obtained by Will was about 65 per cent. of the theoretical, but Schüpphaus got 80 to 81 per cent.[3]

Another method is to nitrate 100 g. glycerine with 500 g. mixed acid of the composition: HNO_3, 23 per cent., H_2SO_4, 68 per cent., H_2O, 9 per cent., at a temperature not exceeding 20°. The mixture is poured into ten times its volume of water, the few oily drops of trinitro-glycerine are separated, and the dinitro-compound is shaken out with ether. The ethereal solution is neutralized by shaking with 5 per cent. soda solution; the ether is distilled off, and the residue dried over sulphuric acid. The yield is about 45 per cent. of the theoretical.

It may also be prepared from trinitro-glycerine by dissolving in sulphuric acid, diluting with water and shaking out with ether.

[1] *See* Escales, *S.S.*, 1906, p. 23; Novak, *ibid.*, p. 191

[2] *B.*, 1908, p. 1107; *S.S.*, 1908, p. 324.

[3] *S.S.*, 1910, p. 361.

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There are two possible isomerides, $CH_2(NO_3).CH(OH).CH_2(NO_3)$ and $CH_2(NO_3).CH(NO_3).CH_2(OH)$, and the product was indeed found to be a mixture. By cooling, about two-thirds of a crystalline modification could be separated, the crystallization being much facilitated by introducing a crystal from a previous experiment. The residual oil, which probably contained both isomers, could not be made to crystallize. The crystals were found to have the composition $3(C_3H_6O_7N_2) + H_2O$. The water was retained on recrystallizing from water, alcohol, ether and benzene, but was given off when the substance was dried over sulphuric acid or in the air at 40°. It was reabsorbed from the air at the ordinary temperature. The liquid portion contained about the same proportion of water (calc. 3·19 per cent.). The crystalline dinitrate readily yields well-defined esters, in which the third hydroxyl group has been replaced by another radicle. Thus the benzoyl ester is obtained by treating it with the calculated quantity of benzoyl chloride and alkali in aqueous solution; it is insoluble in water, crystallizes well from organic solvents and melts at 67°. The p-nitro-benzoyl ester crystallizes still better, and melts at 94°.

The liquid dinitrate has not the same tendency to give well-defined esters. The p-nitro-benzoyl ester was, however, obtained crystalline; it melts at 81° and differs from the compound yielded by the crystalline dinitrate, in that it is readily soluble in hot alcohol, whereas the latter is only slightly soluble. This affords a means for estimating the amount of the two nitrates present in a mixture.

Mononitro-glycerine can be made by nitrating glycerine, carefully neutralizing the remaining acid, and allowing to stand. After a time the mononitrate separates in crystalline form. Crystallization can be accelerated by cooling and rubbing with a glass rod. It melts at 58° to 59° when purified by recrystallization. It does not contain water of crystallization. Unlike the dinitrate it is not explosive. With calcium nitrate it forms a compound $4C_3H_5(OH)_2(NO_3) + Ca(NO_3)_2$, which, after being recrystallized several times from alcohol, melts at 117°.

The mononitrate obtained as above is the α-compound with the nitro-group attached to one of the end carbon atoms, $CH_2(OH).CH(OH).CH_2(NO_3)$, as is shown by the fact that it yields both dinitrates when nitrated further. Moreover, the same compound, melting at 58°, is obtained by the prolonged action of hot water on mono-nitro glycid $CH_2.CH.CH_2(NO_3)$.

$\backslash O /$

The β-mononitrate $CH_2(OH).CH(NO_3).CH_2(OH)$ was also obtained from the mother liquors from the α-nitrate. It melts at 54°. On further nitration it yields only the fluid dinitrate, together with trinitrate. The following Table gives the principal properties of these compounds:

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	Glycerine	Mononitrate	Dinitrate	Tri-nitrate
Spec. grav. (15°) . .	1·27	1·40	1·47	1·60
Melting-point . . .	17°	α 58° β 54°	α-hydrate 26° β-hydrate liquid.	Labile mod. 2·2° Stable mod.12·2°
Boiling-point (15 mm.) .	150–160°	155–160° both isomers	About 145° both isomers	Evaporates rapidly at 160°[1]
Solubility in water at 15°	Unlimited	70 per cent.	7·7 per cent.	0·16 per cent.
Sensitiveness, 2 kg. falling wt.	0	0	Dry 7–10 cm. Crys. or liquid with 3 per cent. H_2O 30 cm.	Less than 4 cm.
Heat of explosion . .	—	—	Dry 1250 cal.	1600 cal.
Heat of combustion (H_2O liquid)	4317 cal.	α 2812 cal.	α dry 2088 cal. α crys. 1986 cal. β 2055 cal.	1600 cal. 1570 cal.
Gelatinising power . .	—	nil	Good	Good
Hygroscopicity . .	80 per cent.	50 per cent.	11 per cent.	0·2 per cent.

The following additional particulars have been given by Blochmann : [2]

	Di-nitrate	Tri-nitrate
Heat test (zinc iodide-starch paper at 70°) .	8 mins.	More than 20 mins.
Ignition point	167°	180°
Velocity of detonation, liquid . . .	1525 m./sec.	1525 m./sec.
,, ,, gelatinised . .	3320 m./sec.	7000 m./sec.
,, ,, with 25 per cent. Guhr	4290 m./sec.	6820 m./sec.

A great disadvantage of dinitro-glycerine is its solubility in acids and water, which makes its separation and purification difficult. It is more liable to become solid than the trinitro-compound and is more difficult to thaw. Hence it does not appear to possess any advantages except as an addition in small proportion to nitro-glycerine in order to lower its freezing-point.

Dinitro-glycerine is a constituent of Tremonit and Ammon-tremonit, explosives that are authorized for conveyance by rail in Germany.[3]

In admixture with trinitro-glycerine the dinitro-compound may be estimated from a determination of the nitrogen in the nitrometer, or by determining the nitric radicles by Silberrad's method (p. 567).

[1] Trinitro-glycerine would probably boil at about 195° under a pressure of 15 mm. if it could be prevented from decomposing.

[2] *Der Bergbau*, August–September 1905 ; *S.S.*, 1906, p. 80.

[3] *See also* Volpert, *S.S.*, 1906, p. 167.

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GRAPHITE

Graphite used in the manufacture of smokeless powder should be quite free from sulphides and free acid, and should contain only a trace of silicate. It should be in the state of fine powder, and should be washed with soda before use.

HEXANITRO-DIPHENYLAMINE

$C_{12}H_4(NO_2)_6.NH$

This is made by nitrating diphenylamine or dinitro-diphenylamine.[1] It is purified by washing with nitric acid and then with water. It is insoluble in ether, benzene, alcohol, etc., and only slightly soluble in acetone ; the best solvent is strong nitric acid. It is a yellow powder, and has a decidedly acid character. The ammonium salt has long been used as a dye under the name of "aurantia." As an explosive it resembles picric acid, trinitro-toluene and tetranitro-methyl-aniline, but is more sensitive than any of them.[2] It is not suitable for use by itself, but must be mixed with other materials to reduce the sensitiveness. It cannot be melted, but it decomposes at 240° to 250°. It possesses the great disadvantage of being very poisonous.

KIESELGUHR

(GUHR, INFUSORIAL EARTH)

(*See* Chapter XXII)

Before use it is ignited and passed through a fine sieve. When mixed with three times its weight of nitro-glycerine it should form a dry plastic mass, from which the nitro-glycerine cannot be pressed out. Under the microscope it is seen to consist of diatoms ; the absorptive power depends largely on the proportion of tubular forms. As the ignited guhr is non-volatile and insoluble in water and organic solvents, its determination presents no difficulty.

MERCURY

Metallic mercury, and such of its compounds as are liable to be reduced to the metallic state during the manufacture and storage of explosives, have a very decided masking effect on the Abel heat test, and for this reason the addition of such mercury compounds is absolutely prohibited in England. In Germany it has been customary to add sufficient mercuric chloride to

[1] *See* Carter, *S.S.*, 1913, pp. 205, 251. [2] *See* Langenscheidt, *S.S.*, 1912, p. 445.

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nitro-cottons to entirely mask the test. The late Dr. Dupré and his sons have worked out spectroscopic tests to be applied to the various explosives; in doing so they have kept in mind that minute traces of mercury are liable to be introduced into explosives during the course of manufacture from the sulphuric acid used and other sources, but that it is only desired to detect mercury in such quantities and in such forms as would affect the heat test. It is calculated that $\frac{1}{1000}$ mg. of mercury is sufficient to mask the heat test, but there would be no great difficulty in devising tests that would detect much smaller quantities. Since they published their methods in *A.R.*, 1907, p. 17, many other chemists have described processes for effecting the same object, but in many cases the essential point just mentioned has not been taken into account by them. The following are the Duprés' methods:

Home Office tests for mercury.

The apparatus consists of two stoppered tubes of about 20 c.c. capacity, joined by a capillary-tube. To one stopper is attached a tube fitted with a good tap. All the grinding must be done very perfectly so as to keep a vacuum for some hours even at a slightly raised temperature. About the centre of each tube, electrodes, contained in tubulars slanted up so as to prevent the entrance of explosive material, are attached. The parts of the tubes below these tubulars are filled with the substance to be examined, the stoppers are replaced, and the tube exhausted by means of a good pump (not a mercury pump). The parts of the tube containing the explosive are then immersed in hot water (about 90°), and a discharge from a powerful induction coil (6-inch spark) passed through it. The capillary tube is then examined end on: if a condenser is used, the spectrum is greatly intensified. If mercury or a volatile mercury salt be present even in very minute quantities, the characteristic lines of the mercury spectrum are seen in addition to those of any other gases that may be present, such as nitrogen, oxygen, and hydrogen. The spectrum of nitrogen may be eliminated by passing a stream of hydrogen through the cold tube before exhausting; after exhaustion, practically only the spectra of mercury, if present, hydrogen and oxygen will then be seen. The hydrogen and oxygen spectra can never be eliminated, as it is impossible to get rid of the last traces of moisture, but this does not in any way interfere with the spectrum of mercury.

The lines relied on for proving the presence of mercury are the two yellow, the green, and the violet of the following wave-lengths: the yellow 5790 and 5769, the green 5461, and the violet 4359. The presence of mercury is not certified, unless all these lines are seen. All the apparatus used, tube, connexions, etc., must be carefully tested to prove the absence of mercury before each test is carried out.

Ungelatinized gun-cotton.

In the case of nitro-cotton about 2 g. of the nitro-cotton, carefully dried at a temperature not exceeding 120° F. (49°), are introduced into the special vacuum tube, and the test is carried out as described above.

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With blasting gelatine, gelignite, &c., about 4 g. of the explosive are ground up with French chalk, introduced into the vacuum tube and tested as above. If the explosive contains a considerable amount of moisture, the introduction of a piece of calcium chloride above the explosive in each limb may be of considerable value. Blank experiments must be made with the chalk used before the test is carried out. **Blasting gelatine, gelignite, etc.**

In order to apply the test to cordite, 15 g. of the cordite are ground so as to pass through the finest sieve of the heat-test set, and extracted with ether for two hours. The flask is then removed, and a carefully cleaned flask substituted; fresh ether is introduced and the extraction continued for a further ten hours. The ether is then distilled off, and the flask carefully dried at a low temperature. The flask is washed out with several quantities of distilled water, a little hydrochloric acid being added to the first boiling. The washings are put into a previously ignited platinum dish, and the solution electrolysed overnight, using the dish as anode and a coil of platinum or gold wire as kathode. Two Leclanché cells are used in series for the electrolysis. The wire is then washed with water and acetone, dried at a low temperature, dropped into a clean narrow test-tube (3 inches by $\frac{3}{8}$-inch), and the part of the tube containing the wire strongly ignited. The bottom of the tube is cut off after removing the wire, and the remainder dropped into the vacuum tube and tested for mercury, as already described. **Cordite.**

Hard gelatinized nitro-cotton preparations are treated exactly as cordite, unless the explosive contains nothing which is soluble in ether, other than a mercury salt, in which case the preliminary two hours' extraction with ether is omitted. **Hard gelatinized nitro-cotton preparations.**

If an ungelatinized nitro-cotton has to be tested for very minute traces of soluble mercury salts, any desired quantity can be extracted with ether, and treated as described above for hard gelatinized nitro-cotton explosives. **Specially delicate tests.**

All the above tests, in which extraction by ether is employed, are of course only tests for soluble mercury-salts, not for metallic mercury. The following very delicate test may be used for blasting gelatine or any other explosive when only metallic mercury is sought. **Metallic mercury.**

Fifteen grammes or any other quantity, according to the degree of delicacy required, are ground up with French chalk and introduced into a stoppered bottle. A piece of silver foil is ignited in a combustion tube, through which a slow current of hydrogen is passed. This foil is then placed in a glass spoon on top of the explosive, and the bottle is tightly stoppered and kept at a temperature of 90° to 100° for ten to fifteen hours. The silver foil is then treated in the same way as the coil in the cordite test.

Considerable difficulty has been experienced by firms who have been using mercury in their explosives in the past in getting their plant free from all traces

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of it. Even six months after the last addition of mercury the explosive still contains enough very seriously to affect the heat test. In this connexion it may be of service to point out what an extremely minute amount of mercury may affect the result. From quantitative experiments it was found that even 0·001 mg. of mercury can combine with as much iodine as would be liberated by an average sample of blasting gelatine in the five minutes after the standard tint on the test-paper was reached, or, in other words, is capable of masking the heat test to the extent of five minutes.

With reference to the rejection of explosives on account of their containing mercury, it has been suggested that the main objection to its use, viz., its effect on the heat test, might be overcome by introducing a piece of silver foil into the tube during the test. It was alleged that the mercury was thus retained entirely by the silver and that the true test of the explosive was obtained. This point was therefore investigated, but it was found that, although the effect of the mercury on the test-paper was undoubtedly counteracted and a test that had been much prolonged by the presence of mercury was considerably shortened, yet the silver itself had a considerable masking effect, probably due to absorption of the acid vapours by the silver. It was therefore considered that, although the above test might be useful as a supplementary test for the presence of mercury, it could not be considered to remove the objections to the use of mercury in explosives. The use of gold foil was also suggested, but although preferable to silver for use with nitrocottons, in that its masking effect is considerably less, yet, as it decomposes nitro-glycerine vapour, it cannot be used with nitro-glycerine explosives.[1]

Microscopic test for mercury.

Hargreaves and Rowe, of the Government Laboratory, South Australia, have worked out a process in which the microscope is used instead of the spectroscope.[2] One hundred g. of blasting gelatine, gelatine dynamite, gelignite, etc., are ground up in a mortar with 100 g. of purified French chalk, the grinding being done in small quantities at a time. The mixture is placed in a flask in a water-oven and connected by glass tubing passing out of the water-oven to a Woulff's bottle or other absorption apparatus containing 50 c.c. of water and 75 c.c. of strong sulphuric acid, and the whole is gently aspirated, while the flask is heated in the bath to the temperature of boiling water. In about two hours the mercuric chloride will be transferred to the dilute sulphuric acid in the absorption apparatus. The solution is then subjected to electrolysis, a pure gold kathode and platinum anode being used. The current required is about 0·5 ampere, or less, at a pressure of 2 volts. The deposition of the mercury on the gold is complete in a few hours, but the current may conveniently be left going all night. When the quantity of mercury is large, the gold kathode will be seen to be coated with mercury, and it may be weighed, and the test thus made quantitative, but, as a rule,

[1] *See also* Florin, *S.S.*, 1911, pp. 21 and 63.

[2] *J.S.C.I.*, 1907, vol. 26, p. 813.

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there will not be sufficient deposit to be visible. The gold foil is removed from the electrolyte, while the current is still running, washed in distilled water, then in alcohol, dried, rolled into a cornet, and inserted into a glass tube 6 mm. in diameter, sealed at one end and expanded at the other and ground flat to fit closely against a glass microscope slide. The glass tube is fitted in a hole in a stout brass plate and then very gently heated, after a dry microscope slide has been placed on top. A sublimate will be obtained on the glass slide, and care must be taken not to raise the temperature sufficiently to revolatilize this. The slide on being examined under the microscope at a magnification of about 250 diameters by transmitted and reflected light will show globules of metallic mercury of large or small size, according to the skill with which the heating has been conducted. If the globules are very small, they may not be readily recognized as mercury, but under the conditions of the method any small opaque dots showing brilliant specks by reflected light must be mercury, and a repetition of the test will probably show larger globules. A similar method has been adopted in West Australia.[1]

In the German Ordnance factories the following test is applied :[2] 2 g. of moist nitro-cotton containing 25 to 30 per cent. water are put into a test-tube 16 mm. wide and 125 mm. long, closed with a cork, through which passes a glass rod covered 5 mm. below the cork with a strip of gold leaf 12 mm. wide. The test-tube is placed in a water-bath heated to 80°, so that the moisture condenses in the neighbourhood of the gold leaf. The heating is continued for at least four hours. If mercury be present, small greyish-white specks will appear on the gold, and for confirmation these should be converted by means of iodine into iodide of mercury. It is advisable to carry out three or four tests simultaneously.

MINERAL JELLY

(PETROLEUM JELLY, VASELINE)

This is a semi-solid product obtained from petroleum : after the greater part of the oil has been distilled off, the residue is drawn from the still, and the paraffin-wax is removed from it as far as possible by filtration. It is a very complex mixture of substances, mostly hydrocarbons, some of which are unsaturated. Mineral jelly is a constituent of cordite and a number of other smokeless powders, and is also added sometimes to blasting explosives.

It has no definite melting-point, and yet in order to obtain a uniform product it is necessary to determine it by some arbitrary method ; it may be done as follows : A rod is provided with a platinum loop somewhat resembling those used for the heat test, but rather larger. A thin filament of the jelly

[1] *See A. and E.*, August, 1908 ; *S.S.*, 1909, p. 191.

[2] Kast, *Spreng- und Zündstoffe*, p. 929.

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is laid across the loop near its upper end, and the rod, together with a thermometer, is introduced into a test-tube, which is placed in a beaker of water. The temperature is gradually raised, and the thermometer is read when the jelly runs down to the bottom of the loop. This is taken as the melting-point. For the manufacture of cordite, it is required that it shall not melt below 30° (86° F.). Its flash-point by the close test should not be below 204° (400° F.), and its specific gravity at 37·8° (100° F.) not less than 0·87. It must be free from scales or specks, and from acidity towards litmus. Heated on a boiling water-bath for twelve hours in an open basin it must not lose more than 0·2 per cent. When burnt off it must leave practically no residue.

Mineral jelly is readily soluble in ether, petroleum ether, and various other organic solvents, but it is only slightly soluble in alcohol; in a mixture of 4 parts methyl-alcohol and 1 part water it is practically insoluble, as also in glacial acetic acid. These last solvents may be used to separate it from nitro-glycerine in the ether extract obtained in the analysis of a complex explosive. After distilling off the ether, some 80 per cent. methyl-alcohol is added to the residue in the flask, which is then heated on a boiling water-bath. The liquid is allowed to settle for a minute or two, and is then decanted through a small filter or directly into a clean beaker. After repeating this operation about four times the mineral jelly is quite free from nitro-glycerine. After the first washing, it is advisable to heat the flask again before adding more alcohol, in order to cause the mineral jelly to adhere to the glass. If any globules of mineral jelly get into the filter or beaker, they must be washed free from nitro-glycerine, and then transferred back into the extraction flask, if necessary with the aid of a little ether. After drying in a steam-oven the mineral jelly may be weighed in the extraction flask.

In old cordites the mineral jelly is often partly converted into substances which are soluble in the 80 per cent. methyl-alcohol, and consequently the percentage found is low.

MOISTURE

(VOLATILE MATTER)

All explosives that have been wholly or partly gelatinized retain more or less of the organic solvent used. In the case of the larger sizes of "Cordite M. D." it amounts frequently to more than 1 per cent., and nitro-cellulose powders, in which there is no nitro-glycerine, generally contain several per cent., which it is impracticable to drive off in the drying stoves, as it is retained by the colloid with great obstinacy.

In the case of explosives not containing nitro-glycerine, camphor, or any other constituent that is slightly volatile, the material is ground and sifted, and 2 g. are weighed out on to a watch-glass and dried in an oven at a suitable

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temperature to constant weight. As a rule, it is not advisable to take for this purpose material that has been ground more finely than is laid down in the directions for the heat test, because the very fine material loses a considerable proportion of its volatile matter during grinding, sifting and weighing. The temperature of the oven is usually somewhere between 65° and 100°. Explosives that are thoroughly stable will withstand the latter temperature for several hours without undergoing a sufficient amount of decomposition to affect the results. In the case of unstable materials a lower temperature must be employed, however, and in extreme cases the drying should be carried out at the ordinary temperature in a vacuum desiccator.

American method.

In order to avoid losses during grinding and weighing, in the United States the nitro-cellulose powder is merely cut up and is degelatinized by dissolving in ether-alcohol and reprecipitating with water.[1] Slices are cut from at least 5 average grains in the case of large-calibre powders; with smaller powders whole grains may be taken or slices may be cut from a number. The sample thus obtained is thoroughly mixed and 1 g. is weighed out. This is dissolved in 150 c.c. of ether-alcohol (2 : 1), and when solution is complete, the nitrocellulose is precipitated by the gradual addition of a suitable amount of water, and the mixture is evaporated on a steam-bath. When evaporation is apparently complete, it is dried for one hour at 95° to 100°, or in a vacuum drier at 50° and weighed. The loss of weight corrected for the residue in the solvent and water used is called the "total volatiles, as packed."

"Moisture" is also determined. This is estimated by drying at least 5 grains, weighing not less than 20 g., for two hours in a vacuum drier at 50° to 60°. The difference between the "total volatiles" and the "moisture" is called the "residual solvent." In the American small-arms powder the "total volatiles" must not exceed 3·15 per cent.

French method.

In France a similar method is used for determining the volatile matter in Poudre B.[2] But if it contain diphenylamine, which is slightly volatile, the estimation is made by drying *in vacuo* at the ordinary temperature.

Determination of water.

For the determination of the water only, in substances which also contain acetone and other volatile compounds, Dupré recommends the use of calcium carbide.[3] The ground material is put into a tube 1 cm. wide and 10 cm. long and covered first with a layer of dry sand and then with a layer of carbide 5 cm. high. The tube is connected to a nitrometer filled with saturated brine, and heated in a water-bath to 100°. The moisture reacts with the calcium carbide producing acetylene. The volume of gas evolved is slightly less than that calculated, when known volumes of water are present; it varies somewhat with different samples of carbide. The coefficient of the carbide may be determined by an experiment with a known weight of pure ammonium

[1] Weaver, *Military Explosives*, 1912, p. 200.
[2] Buisson, *S.S.*, 1913, p. 288.
[3] *Analyst*, 1906, p. 213.

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oxalate, which contains 12·67 per cent. of water of crystallization. The carbide used by Dupré gave 1 c.c. for 0·001725 g. water.[1] If the smokeless powder be exposed to the air, the amount of water in it varies with the hygrometric state of the atmosphere and therefore with the season of the year.[2]

Moisture in nitro-glycerine explosives.

In determining the moisture in nitro-glycerine explosives the difficulty to be overcome is owing to the fact that nitro-glycerine itself is slightly volatile. But investigations carried out at the Royal Gunpowder Factory, Waltham Abbey, by Dupré and Marshall, showed that the difficulty could be overcome by the use of a special apparatus, consisting of an aluminium dish covered with a glass cone, so as to leave only a very slight space between them for the escape of the vapour of water and organic solvent.[3]

Fig. 133.

Apparatus for the Determination of Moisture in Nitro-glycerine Explosives

The apparatus (Fig. 133) is warmed and allowed to stand for half an hour in a desiccator to acquire constant weight. Then 5 g. of the sample are placed in the aluminium dish, the glass cone is put over it, and the whole is weighed. The apparatus is then stood upon a metal plate heated below by boiling water or steam: the top of an ordinary boiling water-oven is suitable. Here it is allowed to stand until the weight is practically constant. In the case of "Cordite, Mark I," or ballistite, or blasting gelatine an hour is sufficient; "Cordite M. D." requires two hours. The apparatus is then removed to the desiccator, allowed to stand for half an hour and weighed. The loss of weight is the amount of moisture (volatile matter) in the explosive taken. Any nitro-glycerine that is driven off from the powder by the heat is condensed on the glass cone; the loss of nitro-glycerine from the apparatus is less than 0·01 per cent. The results are very consistent. The material should be ground and sifted in the same manner as is laid down in the instructions for the heat test.

The U.S. Bureau of Mines determines the moisture in dynamites by placing 2 g. of the explosive on a 3-inch watch-glass in a desiccator containing strong sulphuric acid at about 20°, and weighing after three days. An approximate determination may be made by desiccating in this way for twenty-four hours and multiplying the loss in weight by the factor 1·111. Or the loss of weight in a vacuum desiccator in twenty-four hours may be taken without correction as the approximate amount of moisture.[4]

[1] *See also* Huntly and Coste, *J.S.C.I.*, 1913, p. 63; and Campbell, *ibid.*, p. 67.
[2] *See* Hansen, *S.S.*, 1911, p. 461.
[3] *See* Marshall, *J. Soc. Chem. Ind.*, 1904, vol. 23, p. 154.
[4] *Bureau of Mines Bulletin*, No. 51, p. 29.

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NITRATES

Saltpetre

(NITRE, POTASSIUM NITRATE)

(*See* Chapter IV)

Impurities.

Chlorides should always be tested for, as their presence greatly increases the tendency of the gunpowder or other explosive to deliquesce. In England not more than 0·005 per cent., reckoned as sodium chloride, is allowed; in Germany and France about twice as much. The test is carried out by adding a few drops of silver nitrate solution to a concentrated solution of the saltpetre of known strength, and the opalescence is compared with that given by a solution containing a known amount of sodium chloride.

Sulphates are tested for with barium chloride, calcium with ammonium oxalate and ammonia, and magnesium with ammonium phosphate after removing calcium. The substance should dissolve in water practically without residue, and the solution should be neutral to litmus. To test for sodium nitrate, make a hot saturated solution, allow to cool, dip a platinum wire in the mother liquor and put it in the Bunsen flame; there should be no yellow coloration of the flame. Moisture may be determined by heating to incipient fusion in a crucible; good saltpetre contains practically no moisture.

Saltpetre should contain no chlorate, as it greatly increases the sensitiveness of explosives made with it. Perchlorates are not so injurious; Dupré found that even 1·21 per cent. perchlorate, although it depressed the temperature of ignition of gunpowder 56°, did not appreciably increase the sensitiveness to friction and impact.[1] The amount of chlorate and perchlorate can be determined by heating 10 to 20 g. of the saltpetre for an hour at 545° in a nickel crucible in a Gilbert furnace. The salt is then dissolved in water and filtered, and the chloride is titrated either with silver nitrate by Mohr's method, or more accurately with ammonium sulphocyanide by Volhard's method. The result must be corrected for chloride present in the saltpetre before heating.[2]

The following method for the determination of chlorates is given in *P. et S.*, 11, 1902, p. 63: 10 g. of saltpetre are dissolved in 50 or 60 c.c. of water, and sufficient silver nitrate is added to precipitate the chlorides. The filtrate is then heated to 90°, and a solution of lead nitrate slightly acidified with nitric acid is added. Turbidity indicates the presence of chlorate, and the amount is estimated by using standard solutions of saltpetre and chlorate. In France the saltpetre must not contain more than 0·01 per cent. chlorate,

[1] *A.R.*, 1902, p. 25.

[2] Dupré, *J.S.C.I.*, 1902, p. 825.

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or 0·1 per cent. perchlorate. Indian saltpetre does not contain these impurities, but that made by the conversion of sodium nitrate from Chile saltpetre often contains a small proportion.

Estimation. In black powder the saltpetre is readily determined, because it is soluble in water and the other two constituents are not. The finely ground charcoal has a tendency to pass through the filter. A convenient method is to weigh out 2 g. into a 100 c.c. flask, dissolve in water, make up to the mark, allow the liquid to settle, draw off 20 or 25 c.c. with a pipette, evaporate to dryness, dry in a steam-bath and weigh. The saltpetre may then be examined for chlorides, etc. If there be other substances present soluble in water, the saltpetre can generally be estimated in the water extract by means of the nitrometer.

Sodium Nitrate (Chile Saltpetre)

That used for the manufacture of nitric acid should contain at least 96 per cent., as determined by the nitrometer or the Schlösing method, and not more than 0·75 per cent. of sodium chloride. If the nitrate is to form a constituent of an explosive it should be purified by recrystallization several times. It may be tested by the same methods as are used for saltpetre, but the requirements as to purity are not so severe.

Ammonium Nitrate

Ammonium nitrate may be tested for mineral impurities by the usual methods. When heated in a crucible it should leave very little residue. It may be detected by the smell of ammonia given off when it is heated with caustic soda, and may be estimated by distilling over the ammonia, collecting it in water and titrating it with acid; or the nitric acid may be determined in the nitrometer. It is very deliquescent, and slightly volatile in the steam-bath.

NITRO-BENZENES

(NITRO-BENZOLES)

Mononitro-benzene, $C_6H_5NO_2$, is a somewhat volatile liquid, boiling at 205° under a pressure of 730 mm. It has a characteristic smell resembling that of oil of bitter almonds, and is used in perfumery under the name of "oil of mirbane." It is made by nitrating benzene, and is used principally for the manufacture of aniline. It is not employed largely in explosives. It is not explosive by itself, but has been used to reduce the freezing-point of nitro-glycerine.

Dinitro-benzene, $C_6H_4(NO_2)_2$, has been largely used in the manufacture of blasting explosives. The meta-compound, which is the one principally

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produced by the nitration of nitro-benzene, melts at 90°. It has the disadvantage that it is decidedly poisonous. Explosives containing it should not be handled with the bare hands, and during all manufacturing operations precautions must be taken to prevent the workers inhaling the dust and fumes.[1]

Trinitro-benzene, $C_6H_3(NO_2)_3$, is obtained by the further nitration of dinitro-benzene. The symmetrical compound (1 : 3 : 5) is that generally made; it melts at 121° to 122° when pure. It has not been used very extensively as an explosive, but its explosive properties were investigated by Dautriche.[2] Its effects are similar to those of picric acid and trinitro-toluene, the density and velocity of detonation are intermediate between those of these two substances.[3]

If it be dissolved in 2 or 3 c.c. of acetone or methyl-alcohol and a few drops of 10 per cent. caustic alkali be added, dinitro-benzene gives a purple-rose coloration, turning to deep claret. Trinitro-benzene under the same conditions gives a rich purple brown.[4]

NITRO-CELLULOSE

(*See also* Part IV, Chapters X, XII, and XIII)

Properties.

The true specific gravity is given by Mosenthal as 1·65 to 1·68.[5] Ordinary compressed blocks containing much water and air have a specific gravity of 1·0 to 1·2, but if highly compressed for blasting purposes it may be as high as 1·4. The compressed material resembles wood pulp. When it has been gelatinized with a solvent it resembles horn. It is slowly saponified by alkalies. It is reduced to cellulose by potassium and ammonium hydrosulphides, sodium stannate, sulphides, polysulphides, and thiocarbonates. It is somewhat hygroscopic. Will showed that if n is the percentage of nitrogen in a sample of nitro-cotton, and h the percentage of moisture it takes up in almost saturated air at 25°, $n + h = 14{\cdot}6 \pm 0{\cdot}1$. Even good nitro-cellulose decomposes at all temperatures, giving off carbon monoxide and nitrogen oxides. The rate of decomposition is doubled for every increase of 5° (Will).

When gun-cotton is to be used for the manufacture of other explosives it is usually moulded in hydraulic presses into blocks of various shapes containing 30 to 40 per cent. of water. When used by itself as a blasting explosive it is compressed strongly until it is as hard as hard wood and contains about 20 per cent. of moisture. That used by the British Government is a nitro-cotton containing 12·8 to 13 per cent. of nitrogen mixed with a little phenol and calcium carbonate to prevent decomposition. Small cylinders of the same

[1] *See* Report to the Home Secretary by Dupré and Smith, 1893.
[2] *P. et S.*, vol. 16, 1912, p 27.
[3] *See* Figs. 93, 94, 95.
[4] *Bureau of Mines Bulletin*, No. 51, p. 18.
[5] *J.S.C.I.*, 1906, vol. 26, p. 443.

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material, but dried, are employed as primers for firing charges of wet gun-cotton. Nitrated cotton yarn impregnated with rubber solution is also used as a priming charge for certain sorts of ammunition.

Nitrogen.

According to the strength and composition of the acids and other conditions of nitration, nitro-celluloses can be obtained with very different proportions of nitrogen and differing in many of their properties. It is possible in the laboratory to prepare a gun-cotton containing 14 per cent. of nitrogen, which almost agrees with the formula for the trinitrate $C_6H_7(NO_3)_3O_2$, but this compound is very unstable and breaks down even on standing at the ordinary temperature for a few weeks, leaving a lower nitrate. On the manufacturing scale it is hardly practicable to produce a nitro-cellulose containing more than 13·5 per cent. of nitrogen, and commercial gun-cotton seldom contains more than about 13 per cent. The gun-cotton used for making cordite is specified to contain 12·8 to 13·1 per cent. Nitro-cottons used for making some other smokeless powders for sporting and military purposes generally contain percentages of nitrogen from 12·4 up to 12·8 per cent. Collodion cotton for blasting gelatine contains 12·0 to 12·3 per cent.; for celluloid, varnish, and artificial silk still lower nitrates are used. Various writers have endeavoured to classify nitro-celluloses according to their chemical formulæ; assuming the celluloid molecule to be of some particular size, $C_6H_{10}O_5$ or $C_{12}H_{20}O_{10}$ or $C_{24}H_{40}O_{20}$, they have divided the nitro-celluloses into tri- and di-nitrates, or penta-, tetra-, and tri-nitrates, etc., but as no definite line can be drawn between the different classes, and products can be obtained with any desired percentages of nitrogen, it is better to specify the nitro-celluloses according to their percentages of nitrogen, solubility in ether-alcohol, and other properties.

Detection of nitro-cellulose.

Practically all propellants contain nitro-cellulose wholly or partly gelatinized. Many of them consist practically entirely of nitro-cotton, and most of them contain at least 50 per cent. The form of cellulose used is almost invariably cotton, but wood cellulose has been employed in the manufacture of Schultze powder and some others. Colloided nitro-cellulose can be recognized by its hard, tough nature; unless mixed with liquid material, such as nitro-glycerine, it is as tough as horn. It may be distinguished from other substances by the fact that it is insoluble in water, alcohol, or ether, but soluble in acetone and ethyl acetate. The various nitro-cottons are distinguished from one another, after isolation, by the percentage of nitrogen and of matters soluble in a mixture of alcohol and ether.

Ungelatinized nitro-cellulose can be recognized by the structure of the fibres, which is almost the same as that of the unnitrated material. There is, however, a distinct difference in colour when the fibres are examined in polarized light.[1]

[1] *See* Ambronn, *Kolloid-Zeits.*, 1913, p. 200.

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Estimation of nitro-cellulose.

Nitro-cellulose is usually estimated by extracting the explosive with one or more of the solvents in which nitro-cellulose is insoluble, and then weighing the residue of nitro-cellulose. The first extraction is nearly always with ether, and in many cases no further extraction is needed. If mineral nitrates are present, a further extraction with water is necessary, and in many cases an extraction with benzene is required to remove organic substances. About 2 g. of the explosive are weighed out into a filter-paper or thimble and extracted in a Soxhlet with ether (specific gravity 0·72). The filter-paper and contents are then dried in a water-oven to constant weight, and the weight of the filter-paper or thimble is deducted. The material used for this analysis should be so finely ground that it passes through the finer sieve of the nest used for the heat test. This material should be allowed to soak in the ether all night and then extracted with it for about two hours.

In some cases, if the percentage of nitrogen in the nitro-cellulose is known, it may be estimated indirectly by a nitrogen determination.

Determination of nitrogen.

The estimation of nitrogen in gun-cotton is generally carried out by means of a Lunge nitrometer provided with a cup and graduated from about 100 to 150 c.c. It is filled with mercury, the bottom of the tube being connected by means of rubber tubing with canvas insertion to a compensating tube. The gun-cotton is dried in a water-bath to constant weight, 0·5 g. or more is weighed out, according to the percentage of nitrogen, precautions being taken that moisture is not absorbed during the weighing, as the material is very hygroscopic. It is then transferred to the cup of the nitrometer, and 5 c.c. of concentrated sulphuric acid are added. The material is stirred from time to time with a small glass rod until it dissolves, which takes about half an hour. Then it is allowed to run into the nitrometer, and is rinsed in several times with sulphuric acid, using for this purpose 10 c.c. The bulb is then shaken vigorously so as to bring the mercury and acid into intimate contact. After a short time nitric oxide is evolved. The shaking is continued for about three minutes until the evolution is practically complete. Then the nitrometer is allowed to stand until the acid and mercury have separated from one another and the shaking is repeated for about one minute. After standing for about half an hour to cool, the volume, temperature and barometric pressure are read, the volume is corrected to N. T. P. and the percentage of nitrogen in the gun-cotton is calculated. In this as in all operations with the Lunge nitrometer the result depends to some extent on the exact method of shaking, and it is only after some practice that the operator can obtain results approaching the theoretical. Beginners generally obtain results which are too low.

Berl and Jurrissen carry out the reaction with acid and mercury in a separate vessel and claim that thereby a more accurate result is obtained.[1]

[1] *Ang.*, 1910, vol. xxiii., p. 241 ; *S.S.*, 1910, p. 61. *See also* Koehler, Margueyrol and Loriette, *Ann. Chim. Anal.*, 1914, p. 129 ; Becket, *J.S.C.I.*, 1914, p. 628.

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The Schultze-Tiemann method is also used extensively in many laboratories for the estimation of nitrogen. It usually gives results 0·1 or 0·2 per cent. higher than the Lunge nitrometer. It is specially useful for the analysis of gun-cottons that have not yet undergone purification by boiling, as the nitrometer gives very low results for these. They evidently contain some unstable impurities, which interfere with the reaction of the mercury. The following are the details of the method as it is carried out at the Dartford factory of Messrs. Curtis's and Harvey :

0·5 g. of the dry nitro-cellulose and 30 c.c. of boiling water are introduced into a flask of about 200 c.c. capacity fitted with rubber cork, through which pass two tubes. One of these leads into the lower end of a graduated tube of 150 c.c. capacity and the other is used to introduce liquid into the flask. Both tubes have rubber connexions which can be closed by means of pinchcocks. Air is expelled from the flask and tubes by boiling the water in it energetically for some time, and the pinchcocks are closed. Then the graduated tube is placed in position ; 20 c.c. of hydrochloric acid and 20 c.c. of strong ferrous chloride solution are boiled up in a test-tube, and then the contents are drawn into the flask, care being taken not to admit any air. A little boiling water is added to wash out the test-tube, the admission tube is closed by means of its pinchcock, the contents of the flask are gently boiled, and the other tube leading to the measuring tube is opened. The gas comes off and passes into the measuring tube, which has been filled with strong sodium hydroxide solution and stands in a bath of the same liquid. The evolution lasts about fifteen minutes. Some more boiling water is then run into the flask to wash down any particles of unattacked nitro-cellulose and the contents are then boiled again, this procedure being continued until there is no further evolution of gas. The orifice of the graduated tube is then covered with the thumb or finger protected with a rubber finger-stall, and removed to a large cylinder containing water, where it is allowed to cool. The tube is adjusted so that the water is at the same level inside and out, the volume of nitric oxide is then read, corrected for temperature and pressure and calculated to percentage of nitrogen.

In both the Lunge and the Schultze-Tiemann methods the nitrogen is measured as nitric oxide, NO. According to theory and the actual measurements of Leduc respectively 1 c.c. measured at 0° and 760 mm. is equal to :

Theory .	·062707 g. N.	log. .	$\bar{2}$·79732	reciprocal .	1·5947
Leduc .	·062764		$\bar{2}$·79772		1·5932

The Dumas method can also be used if precautions are taken to prevent the nitro-cellulose from burning too rapidly : it must be mixed with a large quantity of inert material. The method is, however, seldom used for this purpose.

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Nitron Method. The nitro-cellulose is saponified by boiling with strong caustic soda, to which some hydrogen peroxide is added to prevent reduction. The solution is then diluted, acidified with sulphuric acid, and the nitric acid is precipitated with acetate of " nitron " (diphenylendianilodihydrotriazole).[1]

Solubility of nitro-cellulose.

All nitro-celluloses are soluble in acetone, ethyl-acetate, amyl-acetate, and some other organic solvents.[2] They are all insoluble in water and benzene, and all but the very low nitrated products are insoluble in either pure ether or alcohol except at very low temperatures, although commercial nitro-celluloses give up a small amount of fatty matter to ether, and resinous matter and decomposition products to alcohol. It should, however, be noted that commercial ethers usually contain a small proportion of alcohol, and if an ether of this kind be used, some of the nitro-cellulose will be dissolved. The specific gravity of ether used for extracting fatty matter and nitro-glycerine from nitro-cellulose should not exceed 0·720.

The different nitro-celluloses are characterized by different degrees of solubility in a mixture of ether and alcohol. The highest nitrated products are practically insoluble in the mixed solvents. Gun-cottons containing 13 per cent. of nitrogen give up about 8 or 10 per cent., and as the percentage of nitrogen further falls, the solubility rapidly increases until with nitro-cottons containing about 12·3 per cent. solubility is practically complete. The degree of solubility is not conditioned solely by the percentage of nitrogen, however, but also depends upon the proportions of nitric and sulphuric acid used in nitration, and other details of preparation.[3]

Solubility determination.

The solubility of a gun-cotton in ether-alcohol depends to a certain extent upon the composition of the solvent used and the other conditions. It is, therefore, necessary to describe the exact method of carrying out the test. For testing the gun-cotton used in the manufacture of cordite the English War Department lay down the following rules :

50 grains (= 3·3 g.) of the air-dry gun-cotton are weighed out and transferred to a stoppered graduated cylinder of 200 c.c. capacity. A mixture is made of two volumes of ether to one of alcohol, 60 over proof, and 150 c.c. are poured on to the gun-cotton and occasionally agitated with it for about six hours at 15·5° and then allowed to settle. Seventy-five c.c. of the clear liquid are then transferred to a small weighed flask, the greater part of the ether and alcohol is distilled off, and the remainder is driven off by heating in a drying oven the temperature of which is not more than 49° (120° F.), the drying being continued until the weight is constant. The quantity of soluble matter must not be greater than 12 per cent.

This method cannot fail to give somewhat high results, as the whole of the solvents cannot be driven off in the manner prescribed. This, however, is

[1] Busch and Schneider, *S.S.*, 1906, p. 232.

[2] *See also* Chapter XXI.

[3] *See* Chap. x, and chap. xxi.

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not a matter of importance as the results are only intended to be comparative. A more serious objection to the test is that the results depend very largely upon the nature of the ether used, and no directions are given for selecting it. Methylated ether contains considerable proportions of ethyl-methyl ether and dimethyl ether, which have considerably greater solvent action upon gun-cotton than diethyl ether; and it also contains alcohol and water in various proportions. Constant results can only be obtained, therefore, if each supply of ether is tested upon a standard sample of gun-cotton. But even if two ethers give the same result with one sample of gun-cotton, they will not necessarily give the same result with another, which has been made by a different process.

The English official method given above is intended principally for nitro-celluloses, which are only slightly soluble in ethyl-alcohol; with those that are almost entirely soluble it is better to weigh the undissolved residue instead of the dissolved matter. For the soluble nitro-cellulose used for the manufacture of the United States nitro-cellulose powder the official method is as follows:

1 g. of the finely divided dry sample is treated with frequent stirring in a covered beaker or other suitable vessel with 350 c.c. of a mixture of pure ethyl alcohol and pure ethyl ether, the specific gravity of the mixture to be from 0·748 to 0·750 at 20°. The vessel is kept covered to prevent loss by evaporation. The residue is allowed to settle and the supernatant liquid siphoned off. The extraction with ether-alcohol solution is repeated twice: the insoluble residue is poured into a tared Gooch crucible having a thin asbestos filter, and well washed with ether alcohol. The residue is then partially dried at 80°, and the drying completed by exposure to a temperature of 100° till the weight is constant. The per cent. of insoluble matter subtracted from 100 gives the per cent. of soluble nitro-cellulose, which must be at least 95 per cent. If "soluble nitro-cellulose" is to be determined in a nitro-cellulose containing considerably less than 95 per cent., the determination is made on 0·5 g. or less.

In Germany the following method is used: 2 g. of the fine sifted and well-dried nitro-cellulose are placed in a 500 c.c. stoppered cylinder, 215 c.c. of alcohol (specific gravity 0·816 at 15°) are poured on, 285 c.c. of ether (specific gravity 0·720) are then added, the cylinder is shaken frequently for five hours and allowed to settle. Of the clear liquid, 250 c.c. are withdrawn, about 10 c.c. of water are added, and it is evaporated to dryness. The residue is dried for half an hour at 80° and weighed.[1] The object of adding the alcohol first is to prevent the formation of a gelatinous mass.

For methods used in France *see P. et S.*, 8, i., 135; 6, ii., 16; *Post et Neumann*, 2me ed., 1912, Tome III., Fasc. i., p. 349.

[1] Kast, *Spreng- und Zündstoffe*, p. 930.

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Matter insolubl acetone.

The matter insoluble in acetone consists mostly of unnitrated or very imperfectly nitrated fibres. To determine it, 2 g. are treated with about 150 c.c. of acetone for six or eight hours with occasional shaking. It is then allowed to stand overnight and the clear liquid is carefully decanted off. The residue is washed several times by decantation with acetone, then transferred to a tared filter, washed again, dried in the water-bath, and weighed.

Unnitrated fibre in nitro-cellulose.

Unnitrated fibre is sometimes estimated by repeated treatment with sodium sulphide solution, which attacks the nitro-celluloses, but leaves the unnitrated cellulose unaffected. Lunge and Weintraub, however, found the method unsatisfactory, and recommend instead the use of sodium ethylate, which acts in a somewhat similar manner.[1] The method is specially useful in the case of products which contain a considerable proportion of matter insoluble in acetone.

In 100 c.c. of ordinary alcohol dissolve 3 g. of sodium, and if the liquid is not quite clear, filter. Add 100 c.c. of acetone, and of the mixture set aside, 50 c.c. Into the remaining 150 c.c. introduce about 5 g. of the nitro-cellulose. The action is hastened by warming on a water-bath to 40° or 50° with occasional agitation. In twenty or thirty minutes the action is complete ; the brownish-red liquid is allowed to settle, and decanted through a small filter-paper, and the precipitate is washed by decantation with alcohol to remove any condensation products of acetone. The brown solid is then removed by treatment with water, and the residue is washed, first with hot water, and then with water containing a little hydrochloric acid. If the amount of unnitrated cellulose is considerable or if a high degree of accuracy is not desired, this first treatment may suffice. The cellulose obtained evolves no gas in the nitrometer, but gives a strong reaction with diphenylamine, showing that traces of nitro-cellulose are still present. It may, therefore, be desirable to repeat the extraction. For this purpose the residue is first washed with alcohol to displace the water, and is then washed off the filter with the 50 c.c. of the acetone ethylate solution set aside as above. The remainder of the above treatment is then repeated and finally the cellulose is washed with water, dried at 100°, and weighed. It now only gives a slight blue coloration with diphenylamine. The cellulose residue should only have a very slight brown colour, which may be removed by treatment with bleaching solution. A good nitro-cellulose contains hardly any unnitrated fibre.[2]

Free acid and alkali.

Free acid and alkali may be determined in nitro-cellulose by extracting the finely divided material with hot water, filtering, and titrating in the usual way. Very thorough washing is necessary, as the material has the property of absorbing considerable quantities of acid and alkali. When testing for minute traces it is necessary carefully to examine the water and other materials used.

[1] *Ang.*, 1899, p. 473.

[2] *See also* Kast, *Spreng- und Zündstoffe*, p. 929.

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Nitro-cellulose usually contains more or less calcium carbonate, which has either been added intentionally or has been precipitated from the water used for boiling the material during the stabilization. To determine this, digest a known weight of the sample with a known volume of cold diluted standard hydrochloric acid, filter, wash thoroughly and titrate, using methyl-orange or other suitable indicator.

Discoloration. Really pure nitro-cellulose when ungelatinized is quite white, but it has often a slight brown tint due to oxide of iron precipitated in the fibres during manufacture. When stored in a wet condition, it frequently becomes quite black, especially on the surface, in consequence of bacterial action. The bacteria, however, attack mostly the paper or other organic material in contact with the nitro-cellulose. This discoloured nitro-cellulose generally gives a low heat test.

Ash. The gun-cotton is mixed with paraffin-wax and paraffin oil in a large crucible, and the mixture is set alight, a small flame being kept going underneath. As it burns away, more wax is added from time to time. The flame must not be allowed to come in contact with the gun-cotton itself until it has been broken down by the heat. Finally the crucible is ignited to destroy all organic matter, cooled and weighed.

Microscopic examination. For microscopic examination it is best to embed the nitro-cellulose in Canada balsam or moisten it with 50 per cent. alcohol. In polarized light the fibres appear of various colours depending upon the degree of nitration and conditions of manufacture, and can readily be distinguished from unnitrated cellulose and foreign matter. For details of this and other optical properties *see* Mosenthal, *J.S.C.I.*, 1907, 26, 1 ; also Ambronn, *Kolloid-Zeitschrift*, 1913, 200.

Sulphuric esters. It was shown by Cross, Bevan, and Jenks [1] that during the process of nitrating cotton a small proportion of mixed sulphuric nitric esters of cellulose are formed, and it was demonstrated by Hake and Lewis [2] that these bodies are considerably less stable than the pure nitric esters.

The method of determination adopted by Hake and Lewis was to saponify with caustic soda, add sodium carbonate, evaporate to dryness, ignite, dissolve in water, acidify with hydrochloric acid and precipitate with barium chloride. The method has been criticised adversely by Kullgren,[3] who found that it gave low and erratic results ; and it is in fact impossible to precipitate barium sulphate in the presence of large quantities of alkali salts without incurring many large sources of error,[4] and here the quantity is at least eight times that of the nitro-cellulose and several thousand times that of the sulphuric acid.

[1] *Ber.*, 1901, p. 2496.
[2] *J.S.C.I.*, 1905, vol. 24, pp. 374 and 914 ; 1906, vol. 25, p. 624.
[3] *S.S.*, 1912, p. 89.
[4] *See* Allen and Johnston, *J.Am.C.S.*, 1910, p. 588.

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Kullgren decomposes the nitro-cellulose with hydrochloric acid, evaporates to dryness, and then burns the material in a current of oxygen and absorbs the oxides of sulphur on quartz grains coated with soda. He then dissolves the salts off the quartz, adds a little sodium peroxide to complete the oxidation, and precipitates with barium chloride. The results he obtained, about 1·6 per cent. of sulphuric acid, are so very high that doubt is thrown on the method.

There is no reason why the method, which has been used with success for the determination of sulphur in pyrites and in vulcanized rubber goods, should not be used here. The nitro-cellulose is heated in a covered beaker with concentrated nitric acid (specific gravity 1·5), one or two small crystals of potassium chlorate are added from time to time, the liquid is evaporated to dryness, the residue moistened with hydrochloric acid, which is evaporated off again, then moistened with a little dilute hydrochloric acid, dissolved in hot water and precipitated with a small quantity of a dilute solution of barium chloride. A blank test should be carried out with the reagents, and the result corrected accordingly.

Viscosity of solutions of nitro-cellulose.

In the case of collodion cotton, that is to be used in the manufacture of blasting gelatine, it is necessary that the solution in nitro-glycerine be a stiff semi-solid. Different samples of collodion cotton differ very much as regards this property. A nitro-cellulose which produces a very stiff colloid when a little of it is dissolved in nitro-glycerine, will also yield a very viscous solution when it is dissolved in some other solvent, such as ether alcohol or acetone. It is therefore usual to determine the viscosity of a solution of convenient strength, 1 or 2 per cent., in one of these solvents.

The viscosity of a liquid is generally determined by measuring the time that a certain volume of the liquid takes to flow through an orifice. If r be the radius of the orifice and l its length, p the difference of pressure at its two ends, and V the volume that flows through in time t, then the viscosity η measured in absolute units (centimetre-gramme-second) is given by the equation :

$$\eta = \frac{\pi p r^4 t}{8 l V}$$

In order to obtain reliable results it is necessary that l be large compared with r, that is to say, a narrow tube should be used. The absolute viscosities of solutions of nitro-celluloses of different concentrations have been measured by Baker.[1] The viscosity increases very rapidly with concentration, and even the logarithm of η rises greatly as the concentration is increased.

For the commercial testing of oils it is usual to use a standard instrument, such as the viscometers of Redwood or Engler, in which the time of flow through an orifice is taken under conditions that are accurately defined, and

[1] *J.C.S.*, Trans., 1913, p. 1653.

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Viscosity of solutions of nitro-cellulose.

this time is compared with that taken by a standard liquid, such as rape-oil or water. The Engler viscometer has been used also for the examination of solutions of collodion cottons. The orifices of these viscometers are short, and consequently the results are not converted readily into absolute viscosities. In some works use is made of a rough instrument consisting merely of a 50 c.c. pipette with a mark below the bulb as well as one above it. The time is measured that is required for the level of liquid to fall from the upper mark to the lower one, and this time is divided by the time taken by pure acetone or other standard liquid.

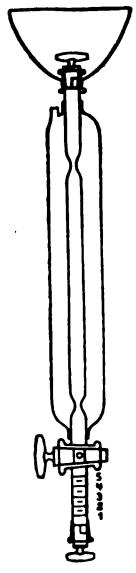

FIG. 134.
Cochius Viscometer

The temperature of the liquid must always be regulated carefully, as the results are much affected by variations of temperature. The solutions must be allowed to stand a day or more before being tested, in order that solution may be complete, and all undissolved particles may settle out. If a particle of undissolved or partially dissolved cotton clog the orifice, the time found will be too long, of course. In order to overcome this difficulty Cochius has devised an instrument in which the relative viscosity is ascertained by measuring the time that a bubble of air of known size takes to ascend through a certain column of the liquid. The instrument is shown in Fig. 134. The inner tube is filled with the liquid under examination, and the size of the air bubble is regulated in the lower graduated portion. By turning the cock through 90° the bubble is admitted to the other part of the tube; the time is measured from the instant the bubble leaves the lower constriction to the instant it reaches the upper one. The tube is surrounded by a water-jacket to facilitate the regulation of the temperature.

The viscosity of a solution does not alter much with time, provided that it be not exposed to light. A high viscosity is considered to indicate that the molecular complexity of the nitro-cotton is great. It has been found by Piest [1] that the addition of 10 per cent. of a solution of a nitro-cotton, that does not give viscous solutions, to a viscous one, causes a very great fall in the viscosity, whereas the addition of 10 per cent. of a more dilute solution of the sample of high viscosity causes a comparatively small fall. In the latter case the viscosity of the mixed solution is about that calculated from the viscosity of the constituent solutions. This phenomenon is consistent with the theory that the liquid really dissolves in the nitro-cotton rather than the nitro-cotton in the liquid.

For making blasting gelatine and other similar high explosives the viscosity should be high, as already stated. For artificial silk, on the other hand, it

[1] *Ang.*, 1913, p. 24.

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should be low ; and for some other purposes, such as the preparation of collodion solution for dipping incandescent gas-mantles, an intermediate value is required.

Fineness.

It is often of importance to ascertain the relative fineness to which nitro-cotton has been pulped. This can be done roughly by examining the material under a lens, but the following test is more satisfactory, as it enables a definite figure to be assigned : 10 g. of the nitro-cotton are placed in a 200 c.c. graduated cylinder, water is added to the 200 c.c. mark, and the cylinder is shaken for three minutes. It is allowed to settle for half an hour, and the volume occupied by the pulp is read off. The finer the pulp the smaller is the volume.

NITRO-GLYCERINE

$C_3H_5N_3O_9 = C_3H_5(NO_3)_3$

(*See also* Chapter XVI)

Properties.

Nitro-glycerine (glycerol trinitrate) is a heavy oily liquid, which when pure is colourless, but the commercial product is pale yellow. Its specific gravity is 1·60 at 15°, but on freezing it contracts 8·3 per cent. of its volume. It is not hygroscopic and is almost insoluble in water. It is also insoluble in glycerine and petroleum spirit, but is readily soluble in ether, ethyl acetate, acetone, ethyl and methyl alcohol, chloroform, glacial acetic acid, amyl alcohol, benzene, toluene, nitro-benzene, phenol, olive oil and sulphuric acid. It dissolves less readily in carbon bisulphide, nitric acid, and hydrochloric acid.[1] At moderately low temperatures nitro-glycerine is liable to solidify. The melting-point of the pure substance is 13·3° ; [2] it crystallizes in the rhombic system. There is also a labile solid modification, which melts at 2·8° (Kast) or 2·0° (Hibbert) and forms crystals belonging to the triclinic system. The melting-point of the commercial product is often some degrees lower than these figures in consequence of the presence of dinitro-glycerine and other substances. (*See also* Chapter XVII.)

Nitro-glycerine is slightly volatile at the ordinary temperature ; at 70° its vapour tension is about 0·005 cm. of mercury, or practically the same as that of mercury itself.[3] Hence it may be concluded that it would boil at about 195° under a pressure of 15 mm. and at 360° at atmospheric pressure, if it did not decompose at temperatures considerably lower. Robertson found that at 125° the decomposition proceeds at such a rate that 2·5 g. give off 1·6 mg. of nitrogen in the form of nitric peroxide, and that this rate is doubled for every rise of 5°.[4] At 145° the evolution of decomposition products is so

[1] *See* Elliott, *School of Mines Quarterly*, vol. 4, p. 15.

[2] Naukhoff, *S.S.*, 1911, p. 124 ; *see also* Kast, *S.S.*, 1906, p. 225 ; Hibbert, *Eighth Inter. Cong. Appl. Chem.*, 1912, vol. 4, p. 37.

[3] Marshall, *J.S.C.I.*, p. 154.

[4] *Seventh Inter. Cong. Appl. Chem.*, 1909, iii B, p. 95.

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rapid that the liquid appears to boil at atmospheric pressure: the gaseous products of decomposition carry over with them nitro-glycerine, nitric acid, water, and other liquid products, which can be condensed.[1] At about 218° nitro-glycerine explodes.

Physiological action. Nitro-glycerine has a very powerful physiological effect. Merely handling it or entering a house containing it will often give a violent headache to anyone not accustomed to it. The best antidote is strong coffee. It is used in medicine either in the form of a 1 per cent. solution in alcohol, "liquor trinitrini," or mixed with chocolate in the form of tablets weighing 5 grains each (0·324 g.) and containing 0·01 grain of nitro-glycerine (0·65 mg.); these are called "tabellæ trinitrini." The dose is $\frac{1}{4}$ to 1 mg. of nitro-glycerine. It is administered to reduce arterial tension in cases of arterial degeneration and chronic Bright's disease, also to relieve difficulty in breathing in cases of asthma, etc. It is absorbed unaltered by the stomach, and is supposed to be converted into nitrite in the body. Its action resembles that of amyl nitrite, but is less rapid and is more prolonged.[2]

Detection. If some of the dry explosive (1 to 5 g.) is placed in a dish on a boiling water-bath, and the dish is covered over with a glass beaker or funnel, after an hour the glass will be found to be clouded with minute drops of nitro-glycerine, if any is present. The appearance is very characteristic, and quite distinct from that of the large drops of liquid which may be formed in consequence of the presence of water or organic solvents.

Nitro-glycerine can also be detected by extracting with ether, evaporating off the solvent, and examining the residue. If the residue is a viscous liquid readily soluble in 80 per cent. methyl alcohol, but insoluble in water, it is probably nitro-glycerine. Absorb some of it in filter-paper and set fire to it. It will burn quietly with a peculiar green flame.

Examination. Nitro-glycerine as such is not allowed to be transported out of the factory at which it is made, and for extra security it is usual to mix it as soon as possible with gun-cotton or some other material which renders it less sensitive. Consequently the examination of commercial nitro-glycerine is hardly ever carried out, except in the factory.

The percentage of *nitrogen* may be ascertained by weighing out 0·32 to 0·35 g. into a small beaker, dissolving it in sulphuric acid and introducing it into the Lunge nitrometer, as described above, under nitro-cellulose. The theoretical percentage is 18·53. The results obtained are often 0·1 to 0·2 per cent. lower than this. If the percentage of nitrogen is very low, it shows the presence of dinitro-glycerine or some other impurity.

To determine the alkalinity take 20 g., shake up with 50 c.c. of water, and titrate with decinormal sulphuric acid, using methyl orange as indicator.

[1] Snelling and Storm, *Bureau of Mines Technical Paper*, No. 12.

[2] *See also* Weinberg, *S.S.*, 1911, p. 427.

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For nitro-glycerine used in the manufacture of cordite, it is specified that the alkalinity shall not exceed 0·01 per cent. calculated as sodium carbonate.

Moisture may be determined by weighing out about 5 g. into a small dish and allowing it to stand at the ordinary temperature over calcium chloride in a desiccator, which may be evacuated if preferred.

Stability Tests. The only test usually applied is the Abel heat test, *q. v.* Guttmann's test cannot be utilized with explosives containing nitro-glycerine.

Estimation of nitro-glycerine.

In consequence of the volatility of nitro-glycerine there is some difficulty in weighing it after extracting it by means of a solvent from a composite explosive. When possible it is therefore estimated by difference, but in many cases it is very desirable to estimate the nitro-glycerine directly. If it is known that no other substance is present, which will evolve nitrogen, or combine with nitric acid in the nitrometer, the percentage of nitro-glycerine can be deduced from a nitrogen determination on the explosive. Or if the amount of nitrogen due to other nitric esters or nitrates is known, it is still possible to calculate the percentage of nitro-glycerine. Almost the whole of the ether can be evaporated off from the ether extract of an explosive without incurring an appreciable loss of nitro-glycerine, provided it be done at a low temperature.[1] The beaker containing the ether solution is placed on a ground glass plate and covered with a bell jar having two tubulars through which pass glass tubes. A rapid current of air dried by means of sulphuric acid is made to enter through one of these tubes, and is delivered downwards about half an inch above the surface of the ether. The air current is regulated so that a marked dimple is made on the surface of the solution. The air and vapour pass out through the other tube, and may be led out of the laboratory window. The current of air should be passed for about six hours. The nitro-glycerine can then be estimated in the residue by means of the nitrometer.

Silberrad, Ablett, and Merryman[2] have worked out a method for the direct estimation of nitro-glycerine which is as follows : A weighed quantity of the ground cordite, or other explosive sufficient to yield 1·5 g. of nitro-glycerine, is placed in a thimble in the extractor A (Fig. 135) which is fitted up as shown. Eighty c.c. of absolute ether is poured into the flask and extraction is carried out in the usual manner. After the extraction is complete, the thimble containing the nitro-cellulose, etc., is washed with a little fresh ether, and removed from the extractor, a little ether being left in the latter. The absorption flasks C, containing 10 c.c. of N/10 acid, are now affixed and excess of sodium ethylate (about 50 c.c. of a solution prepared by dissolving 5 g. of sodium in 100 c.c. of absolute alcohol) is run into the flask little by little through the side tube D. About 10 c.c. of ethylate solution are also

[1] A. L. Hyde, *Bureau of Mines Bulletin*, No. 51, p. 40.
[2] *J. S. C. I.*, 1906, vol. 25, p. 628.

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blown up through the stopcock E, into the extractor. The reaction takes place rapidly and is completed by warming on the water-bath for about six hours, its course may be followed by periodically drawing off small samples by means of the tap E, filtering them and examining them for nitro-glycerine by means of diphenylamine in sulphuric acid. The ether is then distilled up into the extractor and run off by means of the tap, and the apparatus is cleansed of vapour by blowing air through. The residue in the flask is dissolved in water and transferred to a 150 c.c. flask, the washings of the flask and extractor are added, and the volume of liquid is made up to the mark. Fifty c.c. of the solution are then transferred to the flask F, of the reduction apparatus (Fig. 136), 50 g. of a mixture of powdered zinc (2 parts) and reduced iron (1 part) are added together with 50 c.c. of 4 per cent. sodium hydroxide solution, 60 c.c. of N/10 acid being placed in the absorption flasks H. After the apparatus has stood in the cold for one hour, the contents of the flask F are boiled. After boiling for one hour a current of air is passed through for one and a half hours, boiling being still continued. For the last half-hour there should be no water in the condenser. The excess of standard acid is then titrated back. Each c.c. of N/10 acid corresponds to 0·007567 g. of nitro-glycerine. The experimental error does not exceed 1 per cent.

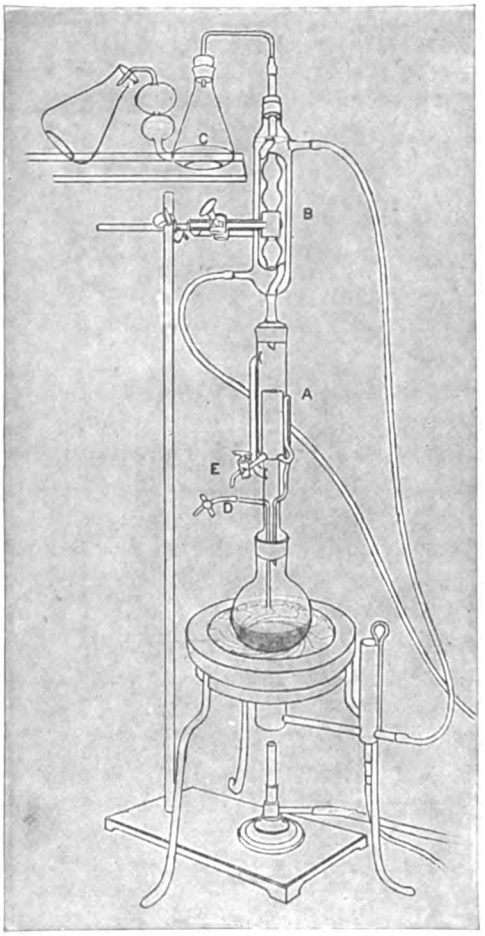

FIG. 135. Apparatus for the Determination of Nitro-glycerine

Separation from nitro-aromatic compounds.

Many blasting explosives contain nitro-glycerine together with a nitro-derivative of an aromatic hydrocarbon, etc. The separate estimation of these substances presents some difficulty, as they are soluble in practically all the same solvents, and nitro-glycerine is slightly volatile. If the mixture obtained consist of nitro-glycerine and di- or tri-nitro-toluene, the nitro-glycerine can be determined by dissolving in sulphuric acid and shaking up in a nitrometer in

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the usual way. The di- or tri-nitro-toluene does not interfere with the reaction to an appreciable extent but if mono-nitro-toluene be present, it is converted into dinitro-toluene, and the nitrometer reading is correspondingly low.[1] Hyde [2] has proposed to separate the nitro-glycerine from the nitro-derivatives by treatment with immiscible solvents, consisting of carbon bisulphide, on the one hand, and a mixture of 65 parts acetic acid and 35 parts water on the other. But the separation is very incomplete even after several extractions, and a large correction consequently has to be made.

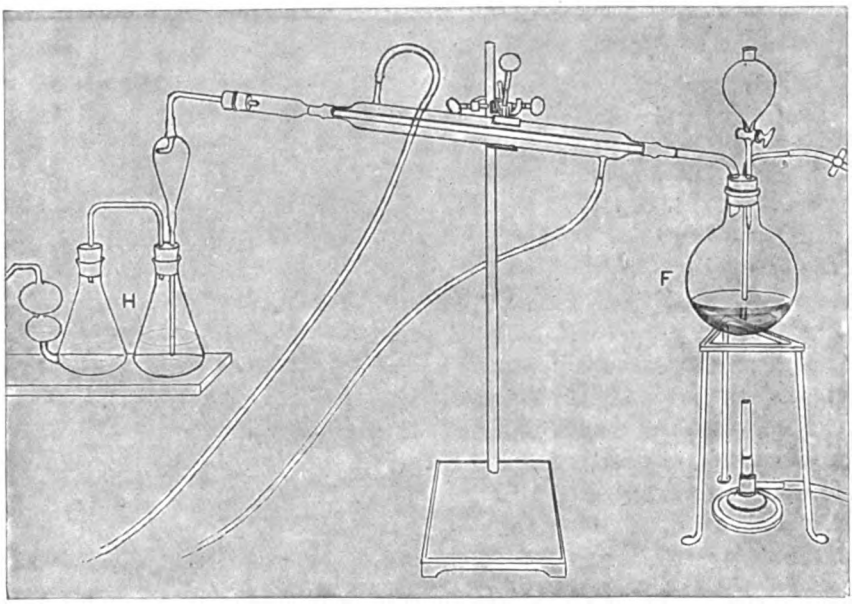

FIG. 136. Apparatus for the Determination of Nitro-glycerine

Estimation of small quantities.

For the estimation of small quantities, such as are used in medicine, Scoville recommends the colorimetric method with phenol-disulphonic acid as used in water analysis.[3] An amount of the alcoholic solution of the substance equivalent to about 0·00065 g. (0·01 grain) of nitro-glycerine is allowed to evaporate spontaneously. If tablets are to be examined, five 0·01 grain tablets are powdered, shaken with 10 c.c. of alcohol for one or two hours, the solution filtered, and 2 c.c. of the filtrate are then treated as above. When dry, 2 c.c. of phenol-disulphonic acid reagent are added, the mixture is well stirred, allowed to stand ten minutes, diluted with water, made slightly

[1] Storm, *Eighth Inter. Cong. Appl. Chem.*, 1912, vol. 4, p. 117.
[2] *Ibid.*, p. 69. *See also J. Am. Chem. Soc.*, 1913, p. 1173; *Ang.*, 1914, vol. ii., p. 85.
[3] *Amer. J. Pharm.*, 1911, p. 359.

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alkaline with potassium hydroxide, and diluted to 100 c.c. At the same time an approximately equivalent quantity of a solution containing 0·7215 g. of potassium nitrate is measured out, evaporated down and treated in the same way, and the colorations, due to the formation of picric acid, are compared. 1·2 c.c. of the standard solution is equivalent to 0·01 grain nitro-glycerine.

NITRO-TOLUENES

When toluene C_7H_8 is nitrated, a mixture of mono-nitro-toluenes is obtained containing about 60 per cent. of the ortho, 38 per cent. of the para, and 2 per cent. of the meta compound. Ortho-nitro-toluene is liquid at the ordinary temperature, whereas the para compound has a melting-point of 54°. They can be separated by strongly cooling the crude product and filtering off the crystals of p-nitro-toluene, or by distilling the mixture *in vacuo*. As there is a considerable demand for p-nitro-toluene, the ortho compound only is taken for further nitration. It can be converted in one stage into trinitro-toluene by the use of a sufficient quantity of a strong mixed acid, but it is more economical in acid, although more laborious, first to form crude dinitro-toluene with mixed acid of medium strength, separate this and then nitrate it further with oleum and nitric acid. After nitration is finished the mixture of acid and trinitro-toluene is allowed to stand until the latter has separated on the surface. The waste acid is run into a tank, and the trinitro-toluene into a vessel of water, where it is granulated by means of a jet of compressed air. It is washed well with warm water, dried and purified by recrystallization either from benzole, or alcohol to which 5 to 10 per cent. of benzole has been added.[1]

Dinitro-toluene

$C_6H_3(NO_2)_2CH_3$

There are a number of isomers known, but that most used for the manufacture of explosives is the 1, 2, 4 compound. This has a melting-point of 70·5° when pure, but a high degree of purity is not generally required, and the product consequently melts at a lower temperature. With other dinitro-toluenes, with mononitro- and trinitro-toluenes it forms addition compounds which melt 30° or 40° lower.[2] As by-products in manufacture complex mixtures are obtained, which are liquid at the ordinary temperature. According to the percentage of nitrogen they contain these are known as liquid dinitro-toluene or liquid trinitro-toluene.

Like dinitro-benzene this substance is decidedly poisonous and precautions should consequently be taken when dealing with it.

[1] *See also* Langenscheidt, *S.S.*, 1912, p. 425; and Will, *B.*, 1914, pp. 704–717.

[2] *See* M. Giua, *B.*, 1914, p. 1718.

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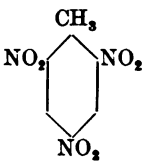
Trinitro-toluene

$C_6H_2(NO_2)_3CH_3$



It is variously called trinol, trotyl, trilite, tritolo (in Italy), and T/N/T. The melting-point of the pure substance is about 81°, that of the commercially pure product a few tenths of a degree lower. The highly purified product is used for filling shells; a less pure product with a melting-point of 77° to 79° is employed in the manufacture of composite detonators, and a still more impure one melting at 72° to 74° as a constituent of many blasting explosives.[1] Water dissolves 0·021 per cent. at 15° and 0·164 per cent. at 100°. Alcohol dissolves 1·6 per cent. at 22° and 10 per cent. at 58°. It is soluble in ether, acetone, benzene, toluene, and ligroin. Trinitro-toluene is somewhat less powerful, less dense and slower in detonation than picric acid, but nevertheless has been able to displace it very largely as an explosive, because it is fairly cheap, does not form sensitive salts as picric acid does, and is less poisonous. **Properties.**

The residue from the mother liquors consists of a complex mixture of various di- and tri-nitro-toluenes; by nitrating this with a mixed acid containing only 15 per cent. of nitric acid Nobel and Co., of Hamburg, obtain a "liquid trinitro-toluene," which has considerable power and has the property of gelatinizing collodion cotton as nitro-glycerine does.[2] It is used in the manufacture of gelatinized explosives. It contains 16·6 to 17·2 per cent. of nitrogen, whereas pure trinitro-toluene contains 18·5 per cent., and dinitro-toluene 15·4 per cent.

Trinitro-toluene is one of the most stable explosives; when heated it does not ignite until a temperature of about 300° is reached and then it does not explode. Even at 150° there is no perceptible decomposition, but at 180° there is a steady though slow evolution of gas.[3] On June 11, 1910, an Order in Council was issued under section 50 of the Explosives Act, 1875, exempting it from being deemed to be an explosive during manufacture and storage, unconditionally, and when conveyed and imported provided it is properly packed. Nevertheless it must not be forgotten that it can explode, and in fact it has caused a number of disasters. In 1906 a fire at the Roburite Factory at Witten led to the explosion of the store-room containing trinitro-toluene and ammonium nitrate; the detonation was so violent that the factory **Accidents.**

[1] *See* Rudolff, *S.S.*, 1907, p. 4.
[2] Ger. Pat. Announcement, 24,235 of September 13, 1910.
[3] Verola, *P. et S.*, vol. 16, 1912, p. 40.

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was almost entirely destroyed, and forty-two people were killed and many injured.[1] In 1908 an explosion occurred at J. W. Leitch and Co.'s works at Huddersfield, whereby five men were injured. The accident was caused by placing a pipe containing trinitro-toluene in a boiler fire to clear the pipe by melting out the contents. In 1909 several men were killed by an explosion in the crystallizing house at Allendorff's factory at Schönebeck, a.E. This accident is somewhat puzzling, as the effects seemed to be too great to be due only to an explosion of vapour, and yet not nearly so great as would have been caused by the explosion of even a small proportion of the trinitro-toluene present in the building.[2] In 1912, 100 kg. exploded from some unknown cause in a cask in the washing house of a German factory, whereby four men were killed and four severely injured. It would seem that the substance is liable occasionally to contain some impurity, which renders it much more dangerous. To a cause of this sort is ascribed a fatal explosion that occurred in 1907 in a vacuum still from which mono-nitro-toluene was distilled.[3] Dupré found that the addition of a little caustic potash caused trinitro-toluene to explode when heated to 160°.[4]

Density. Trinitro-toluene, which has been melted, has a density of 1·57 to 1·60; when powdered and compressed Dautriche found that it had the following densities:

Pressure		Mean density
kg./cm.^{2}	tons/in^2	
275	1·75	1·320
685	4·35	1·456
1375	8·73	1·558
2060	13·1	1·584
2750	17·5	1·599
3435	21·8	1·602
4125	26·2	1·610

whence it is concluded that the limiting density for the compressed material is about 1·62.[5]

Detection. If caustic potash be added to an acetone solution of trinitro-toluene, an intense red coloration is produced; dinitro-toluene gradually gives a blue

[1] *See S.S.*, 1907, pp. 333, 413, and 416.
[2] *See S.S.*, 1909, p. 213.
[3] *S.S.*, 1908, p. 298.
[4] *A.R.*, 1903, p. 26.
[5] *P. et S.*, vol. 16, 1912, p. 28. *See also* Molinari and Quartieri, *S.S.*, 1913, p. 405.

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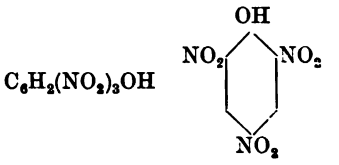
coloration, which, however, is masked by the red colour if there be any of the trinitro-derivative present.[1]

PICRIC ACID

(TRINITROPHENOL)



$C_6H_2(NO_2)_3OH$

Manufacture.

This substance is the final product of the action of nitric acid on a large number of substances containing a benzene nucleus, just as oxalic acid is the result of the oxidation of many bodies of the fatty series. Picric acid is obtainable from indigo, aloes, gum-resins, wool, silk, etc., but the common idea that the yellow colour produced by nitric acid on animal tissues, such as skin, wool, etc., is due to the production of picric acid is erroneous : it is due to the formation of xanthoproteic acid.

Picric acid was formerly prepared by the direct action of nitric acid on phenol, but is now made by first dissolving the phenol in strong sulphuric acid and then acting on the resulting phenol-sulphonic acid with excess of nitric acid. Mono-and dinitro-phenol may result if the action is not carried far enough. Picric acid separates from the acid mixture as an oily liquid, which solidifies on cooling. It is purified by recrystallization from water.[2]

Properties.

Picric acid forms pale yellow, crystalline needles or scales, of an intensely bitter taste and specific gravity 1·777. The pure acid melts at 122·5°, and the common at a lower temperature, to a brownish-yellow oil, which at a higher temperature partially sublimes, and boils with formation of yellow, bitter, suffocating vapours. The lower melting-point of impure picric acid is probably due to an admixture of dinitro-phenols or of a nitro-cresol. Hence the melting-point of picric acid is a test of its purity.

When strongly heated, picric acid burns rapidly with formation of an intensely black smoke. It does not explode when heated under ordinary conditions, but it can be made to explode by allowing it to fall into a tube heated to a red heat. Picric acid can be detonated by means of other violent explosives ; a charge of 1 g. of mercury fulminate suffices to determine the explosion. Metallic picrates, especially that of lead, or even an imperfect mixture of picric acid with the oxides or nitrates, will detonate violently when heated or submitted to a moderate blow, and the explosion under favourable

[1] Storm, *Eighth Inst. Cong. Appl. Chem.*, 1912, vol. 4, p. 123 ; *Bureau of Mines Bulletin*, No. 51, p. 18.

[2] *See S.S.*, 1910, p. 15.

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conditions will induce the detonation of neighbouring quantities of picric acid or picrates, even though they be wet. In spite of the comparative insensitiveness of the pure substance, these properties have led to a number of serious accidents, of which the following were particularly disastrous :

Heron Chemical Works, Lancaster, June 7, 1882.

Roberts, Dale and Co.'s Works, Cornbrook, near Manchester, June 22, 1887.

Rheinan, near Mannheim, June 27, 1890.

Read, Holliday and Sons, Huddersfield, May 30, 1900.

Griesheim-Elektron, near Frankfurt a.Main, April 25, 1901, twenty-four killed and one hundred and seventy-eight injured.

Woolwich Arsenal, June 18, 1903, sixteen killed and fourteen injured.

Picric acid is soluble in about 15 parts of boiling water, but it requires 26 parts at 76° and 86 at 15°. The solution is intensely bitter, bright yellow in colour, and reddens litmus. In a stratum 1 inch in depth, the yellow colour of a solution of 1 part of picric acid in 30,000 of water is distinctly visible. The yellow colour of picric acid solutions is intensified by neutralization with an alkali. A cold saturated aqueous solution of picric acid gives a copious precipitate on adding hydrochloric acid.

Picric acid is readily soluble in alcohol, ether, chloroform, benzene, petroleum spirit, etc. ; the last four solutions being colourless or nearly so. Such of the above solvents as are not miscible with water remove picric acid more or less perfectly from its aqueous solution, or that of a picrate which has been freely acidulated with sulphuric acid. Ether is preferable to chloroform for this purpose. A solution of picric acid in ether gives up the greater part of its colour to water, but on adding sulphuric acid or, still better, hydrochloric acid, the condition is reversed, the picric acid going chiefly into the ether.

All the above solutions of picric acid, including the aqueous, dye silk, wool, skin and other nitrogenous organic matters a yellow colour of a slightly greenish shade. The stain is not removable by water, but soap or alkali partly destroys it. Animal charcoal absorbs a large quantity of picric acid from its aqueous solution. Picric acid is used as a dye for silk and wool, but is employed to modify the shades of other colours rather than as an unmixed dye. Thus with methyl-green it gives yellow-green, with indigo-carmine or aniline-blue a deep green, and with magenta a very fast scarlet. Since the introduction of the yellow azo-dyes the employment of picric acid has decreased.

It is now used extensively as a filler for shells, and has been given various names in different countries when used in this way. (*See* Chapter XXV.)

Detection and estimation of picric acid.

The yellow colour and extremely bitter taste of the aqueous solution of picric acid, the deepening of the yellow colour on adding excess of alkali, and the power possessed by the solution of the free acid of dyeing immersed wool

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or silk yellow are themselves important indications of its presence. In the presence of other colouring or interfering bodies, the picric acid may be extracted from the aqueous solution by agitation with ether or amyl alcohol, after strongly acidulating with sulphuric acid. The picric acid may then be recovered by evaporating the ethereal solution or agitating it with a solution of sodium hydroxide, when it will pass into the alkaline liquid. The extraction of picric acid from an acidulated solution by ether, benzene, or amyl alcohol may be made quantitative.

Picric acid may be titrated with ease and accuracy by standard alkali and phenolphthalein.[1] The process is applicable to the ethereal or benzene solution of picric acid if this be first diluted with alcohol.

An aqueous solution of picric acid is not precipitated on adding neutral lead acetate, but basic or ammoniacal lead acetate gives a bright yellow precipitate even with very dilute solutions of picric acid.[2]

Picric acid is not precipitated from its aqueous solution by copper sulphate; but the ammonio-sulphate produces a bright green precipitate, which is insoluble in ammonia and is decomposed by washing with water. A solution containing 1/10,000 of picric acid gives a distinct precipitate with ammonia-copper sulphate in twenty-four hours.

If a solution of picric acid be treated with zinc and dilute sulphuric acid, a turbid yellowish-red solution is obtained, which, when poured off from the excess of zinc and mixed with alcohol, develops a green colour, changing through blue to a violet.

Picric acid forms highly insoluble compounds with many of the vegetable alkaloids, and the insolubility of the cinchonine salt has been employed for the determination of picric acid. A solution of cinchonine sulphate acidulated with sulphuric acid is added to the picric acid solution. The precipitate of cinchonine picrate, $C_{20}H_{24}N_2O(C_6H_3N_3O_7)_2$, is washed with cold water, rinsed off the filter into a porcelain crucible or dish, the water evaporated on the water-bath, and the residual salt weighed. The yellow, intensely bitter alkaloid berberine, is said to precipitate picric acid so perfectly that, on mixing the picric and alkaloidal solutions in equivalent proportions and filtering, the filtrate is colourless and perfectly free from bitter taste.

Acridine has been suggested by Anschütz [3] as a suitable reagent for the determination of picric acid, the hydrochloride being used as a precipitant for metallic picrates and a solution of the free base in benzene for the picric acid compounds of hydrocarbons.

[1] P. Kay, *Jour. Soc. Dyers, &c.*, vol. 4, p. 84.

[2] If the precipitate is decomposed by dilute sulphuric acid and the filtered solution rendered ammoniacal and evaporated to dryness, a residue is obtained which gives a deep brown colour on heating with potassium cyanide. This behaviour distinguishes picric acid from quercitron and such other vegetable yellow colouring-matters as are precipitated by basic lead acetate.

[3] B., vol. 17, p. 438; *J.S.C.I.*, 1884, vol. 3, p. 324.

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Of the compounds of picric acid with solid hydrocarbons, that with naphthalene, $C_{10}H_8 + C_6H_3(NO_2)_3O$, is almost the only one precipitated when the cold alcoholic solution of the hydrocarbon is mixed with a cold alcoholic solution of picric acid. It forms stellate groups of golden-yellow needles, melting at 149°. The formation of naphthalene picrate may be employed to distinguish picric acid from similar nitro-compounds.

The nitrogen may be determined in picric acid by the Kjeldahl or Dumas method. In the Lunge nitrometer it evolves no gas. Picric acid or a picrate may therefore be estimated by a nitrogen determination.

Examination of picric acid.

The picric acid of commerce is generally crystallized. Though now of much better quality than formerly, it is still liable to contain impurities, and occasionally is intentionally adulterated. Thus sodium sulphate is sometimes added before crystallization, and oxalic acid and sugar are said to be met with occasionally.

General impurities and adulterations may be detected and determined by treating 2 g. of the finely powdered sample with 50c.c. of ether. The picric acid dissolves, while any picrates, nitrates, oxalic acid, boric acid, sodium sulphate, alum, sugar, etc., will be left insoluble, and, after removal of the ethereal liquid, may be readily identified and determined. For the detection and determination of *water* and *oxalic acid*, 50 c.c. of warm benzene may be advantageously substituted for the ether. Sugar and boric acid may be separated from the other impurities by treating the residue insoluble in ether or benzene with rectified spirit. If *boric acid* is present the alcoholic solution will burn with a green flame. *Sugar* may also be sought for by neutralizing the aqueous solution of the sample by sodium carbonate, evaporating to dryness, and extracting with proof-spirit, which will dissolve any sugar and leave the sodium picrate insoluble.

Sulphuric, hydrochloric, and oxalic acids, and their salts, may be detected by adding solutions of barium, silver, and calcium, respectively, to the warm, filtered, aqueous solution of the sample. 0·2 per cent. of SO_3, as estimated by precipitation as barium sulphate, is the maximum proportion allowed by the French Government in picric acid intended for the manufacture of mélinite. *Free sulphuric acid* might be detected by dissolving the sample in warm benzene, agitating the solution with warm water, removing the benzene layer, and again agitating the aqueous liquid with benzene, till all yellow colour is removed. On then titrating the aqueous liquid with standard alkali, the volume required for neutralization will correspond to the free sulphuric or other mineral acid of the sample.

It is possible that commercial picric acid occasionally contains a *nitrophenolsulphonic acid*. Such an impurity would be indicated by the presence of sulphates in the residue obtained on igniting with a large excess of alkali.[1]

[1] *See Analyst*, vol. 13, p. 43.

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A method of estimating small proportions of dinitro-phenol in picric acid is by treating the aqueous solution of the sample with bromine, as proposed by Allen.[1] With dinitro-phenol the following reaction occurs: $C_6H_3(NO_2)_2OH + Br_2 = HBr + C_6H_2Br(NO_2)_2OH$. With picric acid, bromine reacts as follows:

$$C_6H_2(NO_2)_3OH + Br_2 = HBr + HNO_3 + C_6H_2Br(NO_2)_2OH.$$

In each case 2 atoms of bromine enter into the reaction, with formation of a bromo-dinitro-phenol (the same in each case), and 1 molecule of hydrobromic acid. But in the case of picric acid nitric acid is formed in addition, and hence the acidity of the liquid at the end of the reaction would be greater the larger the proportion of picric acid present. If the bromo-dinitro-phenol and excess of bromine [2] were removed by agitation with ether or similar solvent, the acidity of the aqueous liquid could be ascertained with great accuracy by titration with standard alkali.

The reaction between bromine and dinitro-phenol occurs promptly, but in the case of picric acid it is gradual. In twelve hours it is complete, but the change that occurs in the course of a few minutes is negligible. This fact enables the reaction with bromine to be utilized for the direct estimation of the dinitro-phenol, instead of for its indirect estimation (by estimating the picric acid), as when the acidity is ascertained. The following method of operating was found by the author to be the most satisfactory: 1 g. of the sample of picric acid is dissolved in about 100 c.c. of warm water. A saturated solution of bromine in water is diluted with twice its measure of water in a large tapped and stoppered separator, and from this run into a burette. From this burette, a definite volume of the bromine solution, which is approximately of 1 per cent. strength, is run into a flask and an equal measure into another similar flask, both of which are immediately closed. The picric acid solution is then poured into one of the flasks, the last drops rinsed in without delay, and then an excess of a solution of potassium iodide at once added to the contents of both flasks. The liberated iodine is then determined by titration with a decinormal solution of sodium thiosulphate (hyposulphite) in the usual way.[3] From the difference in the volume of the solution required in the two experiments the amount of bromine which has reacted with the dinitro-phenol is easily found. *Dinitro-phenol* reacts with 86·96 per cent. of bromine, taking up 43·48 per cent. *Mononitro-phenol*, if present, which is improbable, would react with 230·2 per cent. of bromine, taking up 115·1 per cent. to form the

[1] *Jour. Soc. Dyers, &c.*, vol. 4, p. 84.

[2] If preferred, before extracting with ether the excess of bromine may be got rid of by adding potassium iodide and then sufficient sodium thiosulphate to react with the iodine liberated.

[3] Allen found iodine to be wholly without action on solutions of either mono-, di-, or trinitrophenol.

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compound $C_6H_2Br_2(NO_2).OH$. Allen has verified these reactions by experiments on specially prepared mono- and dinitro-phenol. When the process is applied to commercial picric acid the results are liable to be somewhat in excess of the truth, owing to slight action of the bromine on the picric acid itself.

For the detection and estimation of trinitro-cresol *see* Kast, *Spreng- und Zundstoffe*, p. 974; Post et Neumann, *Analyse Chimique*, Tome 3, Fasc. 1, p. 392.

Density of picric acid.

Picric acid which has been melted has a density of 1·68 to 1·70. On solidifying there is an apparent expansion which, however, is partly or wholly due to the manner in which it crystallizes: needle-like crystals are formed between which small interstices are left. By compression somewhat higher densities can be attained; Dautriche obtained the following:

Pressure		Mean density
kg./cm.²	tons/in.²	
275	1·75	1·315
685	4·35	1·480
1375	8·73	1·614
2060	13·1	1·672
2750	17·5	1·714
3435	21·8	1·731
4125	26·2	1·740

whence it is concluded that the limiting density for the compressed material is about 1·76.[1]

PICRATES AND TRINITRO-CRESYLATES

The composition and temperatures of ignition of a large number of metallic picrates were investigated by Silberrad and Phillips,[2] and the formation and explosibility of various picrates and trinitro-cresylates by Kast.[3] The picrates of lead, calcium, barium, potassium, and copper explode when heated, the lead compound being much more violent than the others. The picrates of sodium, zinc, silver, magnesium and iron explode with considerably less violence; those of ammonium, mercury and aluminium, like picric acid itself, do not explode when heated in the ordinary way.

The trinitro-cresylates behave very similarly to the corresponding picrates.

[1] *P. et S.*, vol. 16, 1912, p. 28.
[2] *J.C.S.*, Trans., 1908, p. 474.
[3] *S.S.*, 1911, vol. pp. 7, 31 and 67.

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The lead salts are also by far the most sensitive to blows, being about as dangerous in this respect as nitro-glycerine, blasting gelatine and dry gun-cotton. The salts of the other heavy metals, such as copper, silver, iron, calcium, and barium are also somewhat sensitive: more so than picric acid. The salts of sodium, potassium and ammonium are less sensitive, and those containing water of crystallization are less so than the dried substances.

The action of solutions of picric acid and trinitro-cresol upon different metals was investigated by Kast. Plates of metal 5 × 10 cm. were placed in mixtures of 50 g. picric acid or trinitro-cresol and 200 g. water for four weeks. It was then found that the following quantities of the metals had been dissolved:

	Picric acid	Tri-nitro-creso
Lead	3·91 g.	4·15 g.
Iron	13·71 g.	3·78 g.
Zinc	18·86 g.	0·48 g.
Copper	2·37 g.	1·04 g.
Brass	1·19 g.	1·02 g.
Aluminium	small quantity	small quantity

Saposhnikof tried the effect of molten picric acid on metals under conditions more nearly resembling those that prevail in a shell that is filled with the melted explosive. One g. of the finely divided metal was placed in a beaker with 2 g. of picric acid and kept at a temperature of 125° for eight and a half to nine hours. The weights of metal that had been dissolved were:

Lead	0·2798 g.
Iron	0·1530 g.
Zinc	0·2046 g.
Copper	0·1754 g.
Aluminium	0·0488 g.
Nickel	0·1862 g.
Tin	0

Ammonium picrate, $C_6H_2(NO_2)_3ONH_4$, mixed with potassium nitrate in the proportion 43 : 57 is used in the exploders of lyddite shell. Numerous proposals have been made in patent specifications and elsewhere to use other picrates in explosive mixtures, but these have never come into general use.

SULPHUR

(*See* Chapter V)

Impurities. This should be finely ground roll sulphur free from acid, arsenic and ash. To test for acid, boil with water and test with litmus-paper; there should not be more than a very faint reddening. Arsenic gives the sulphur an orange-

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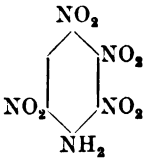
yellow colour; to test for it, 5 g. are treated for a quarter of an hour with 100 c.c. ammonia at 50° to 60°, and the liquid is filtered and acidified with hydrochloric acid: there should be no weighable precipitate even after adding sulphuretted hydrogen water. The residue on ignition should not exceed 0·15 per cent.

Estimation. To determine the sulphur in gunpowder, it is evaporated not less than three times with strong *aqua regia*. The residue is moistened with hydrochloric acid and again evaporated to drive off the nitric acid, then dissolved in water, filtered and precipitated with barium chloride solution, using only slightly more than is actually required. It is not essential to destroy entirely all the carbon in the powder.

Roll sulphur is readily soluble in carbon bisulphide, but flowers of sulphur leave a residue of 20 to 30 per cent. insoluble in this solvent. Sulphur is moderately soluble in acetone, ether, alcohol, and other organic solvents. It may be separated from nitro-glycerine by dissolving the latter in acetic acid of 70 per cent. strength: sulphur is practically insoluble in this solvent.[1] Sulphur oxidizes slowly at 100°, especially if nitrates be present: for the determination of moisture in black powder, etc., the material should not be heated above about 70°.

TETRANITRANILINE

$C_6H_3N_5O_8$



This is made by nitrating aniline.[2] It is claimed that it is more powerful than any other solid explosive. On explosion it leaves no carbonaceous residue. When heated it does not melt, but decomposes at 216° to 222°. To blows it is slightly less sensitive than tetryl, but it is detonated by fulminate with equal ease. Its absolute density is 1·867.

[1] *Bureau of Mines Bulletin*, No. 51, p. 42.

[2] Flürscheim, *S.S.*, 1913, p. 185; Eng. Pat. 3224 and 3906 of 1910; Ger. Pat. 242,079 and 241,697.

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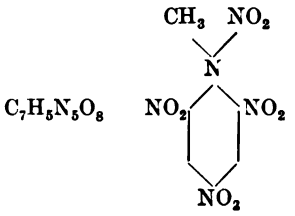
TETRANITRO-METHYLANILINE



This substance is also called tetryl, tetralite, etc. ; it is made by nitrating methyl- or dimethyl-aniline ; [1] 100 kg. of dimethylaniline are dissolved in 1000 kg. of sulphuric acid of 97 to 98 per cent. strength ; 430 kg. of nitric acid of specific gravity 1·48 (87 per cent. HNO_3) are placed in a vessel provided with heating and cooling coils, and heated to 40°. The sulphuric acid solution is then added in a thin stream : an energetic reaction sets in, but the temperature at first must not be allowed to rise above 44° ; when two-thirds of the solution have been added, it may be allowed to rise to 55°. This operation takes eight or nine hours ; when all the solution has been added, the mixture is allowed to stand for a further two hours in order that the nitration may be completed. It is then cooled down and allowed to stand over night. The tetryl separates out in fine crystals on the surface of the acid. The acid can be separated in a centrifugal machine ; after this, the product is washed with water until it is practically neutral. From 100 parts of dimethylaniline about 210 parts of crude washed tetryl are obtained. The nitric acid should not be of greater strength than stated above, otherwise the product separates in large crystals, which cannot be washed so effectively. The washed product is dried and then purified by recrystallization from acetone or 90 per cent. benzole. The melting-point of the pure substance is 129° to 130° ; it is pale yellow in colour. It is used in conjunction with fulminate as a filling for detonators, and as a primer for high explosive shell. Detonating fuse has also been filled with it.

WOOD-MEAL

(WOOD PULP)

Wood-meal is a constituent of gelignite and many other high explosives. It serves the double purpose of absorbing the nitro-glycerine and reducing the temperature of explosion. It should be free from acid and foreign

[1] *See* Vasquez, *Memorial de Artilleria*, September 1910 ; *S.S.*, 1911, p. 302 ; Langenscheidt, *S.S.*, 1912, p. 445.

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substances, especially particles of metal, and should not contain much resin. The moisture should not exceed about 10 per cent. It should absorb nitroglycerine readily. It is recognized by its appearance when examined under a lens or microscope. It gives up a few per cent. of substance when extracted with ether, water, or dilute acid ; it is therefore difficult to estimate it with accuracy.

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APPENDICES

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APPENDIX I

REGULATIONS OF THE IMPERIAL GERMAN RAILWAY COMMISSION

Dangerous goods are divided into the following classes :

I. Explosible goods.
II. Spontaneously combustible goods.
III. Combustible liquids.
IV. Poisons.
V. Corrosive goods.
VI. Goods liable to putrefaction.

Class I is subdivided into :

I*a*. Explosives.
I*b*. Ammunition.
I*c*. Matches and fireworks.
I*d*. Compressed and liquefied gases.
I*e*. Goods which in contact with water give gases that are combustible or support combustion.

Class I*a* is further subdivided into :

A. Blasting explosives.
B. Propellants.
C. Other explosives.

These again are split up into groups according as they satisfy the tests laid down. Different tests are specified for each sub-group, and the results are compared with those given by certain standard substances.

A, group 1 may be sent in unlimited quantities as ordinary goods.
2 quantities of 200 kg. only as ordinary goods.
3 truck loads only.
B, group 1 may be sent in unlimited quantities as ordinary goods.
2 truck loads only.

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The sub-groups with their respective standards are as follows :

Sub-group	Description	Standard
A. 1 (*a*)	Ammonium nitrate explosives	Donarite
1 (*b*)	Organic nitro-compounds	Picric acid
1 (*c*)	Nitro-cellulose with 25 per cent. water or alcohol or compressed with 15 per cent. water.	
1 (*d*)	Nitrate mixtures.	Sprengsalpeter
2 (*a*)	Organic nitro-compounds insoluble in water with 25 per cent. water.	Tetranitro-methylaniline
2 (*b*)	Chlorate and perchlorate explosives.	Cheddite.
2 (*c*)	Nitrated chlorhydrins.	
2 (*d*)	Triplastite.	
3 (*a*)	Organic nitro-compounds not in sub-groups 1 (*b*) or 2 (*a*).	Tetranitro-methylaniline.
3 (*b*)	Nitro-cellulose unpressed with 15 per cent. water, or compressed dry in cartridges, paraffined.	
3 (*c*)	Chlorate and perchlorate explosives not in 2 (*b*).	Silesia I.
3 (*d*)	Black powder, and similar explosives not in 1 (*d*).	Black powder.
3 (*e*)	Dynamite, &c.	Blasting gelatine or Guhr dynamite.
3 (*f*)	Ammonium nitrate explosives not in 1 (*a*).	Gelatine dynamite.
3 (g)	Samples.	Blasting gelatine or Guhr dynamite.
B. 1	Gelatinized smokeless powders satisfying sundry tests.	
B. 2	Gelatinised smokeless powders not satisfying the tests.	
	Ungelatinized smokeless powders.	
	Black powder pressed and granulated, etc.	
	Thoroughly gelatinized cords of powder and articles made from them.	

TESTS

Applied to Explosives by the German Railway Commission

A. Blasting Explosives

I. *Ammonium Nitrate Explosives*

As the standard of comparison *Donarite* is used having the following composition :

Ammonium nitrate	80 per cent.
Trinitro-toluene	12 ,,
Rye flour	4 ,,
Nitro-glycerine	4 ,,

The solid constituents are dried, passed through a sieve with 256 meshes to the

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sq. cm. (40 meshes to the inch), and mixed together, and then with the nitro-glycerine, until the mixture is quite uniform.

The tests consist of :

1. Chemical analysis.
2. Behaviour to litmus paper.
3. Exposure to high temperature.
4. Shaking test.
5. Behaviour on ignition.
6. Sensitiveness to mechanical influence (blows, friction).
7. Addition of water (separation of nitro-glycerine).

Preparation of the explosive. Care must be taken that the sample correctly represents the bulk of the explosive. The sample is to be dried over calcium chloride. It can be reduced to the required state of division in a mortar.

1. *Chemical analysis.* The proportions must be accurately determined, especially of such substances as increase the explosibility of the explosive (*e.g.* nitro-glycerine).

2. *Behaviour to litmus paper.* 1 g. of the explosive is rubbed up with 3 c.c. of distilled water and the mixture is tested with sensitive blue litmus paper. Comparative tests are carried out before and after hot storage (*see* 3). There must be no increase of any acid reaction after the storage. Donarite has a slight acid reaction before and after hot storage.

3. *Storage of the explosive at 75° C.* Two samples of 10 g. each of the undried explosive are to be placed in lightly closed weighing bottles, 35 mm. in diameter and 50 mm. high. The bottles are to be kept for forty-eight hours in a drying oven heated to 75° C. It should then be ascertained whether there is any alteration in the weight of the samples or their condition (appearance, reaction, smell). Donarite only suffers slight loss of weight, and there are no serious signs of decomposition.

4. *Shaking test for separation of ingredients.* 100 g. of the explosive are placed in a dry wide-mouthed bottle of 150 c.c. capacity and shaken backwards and forwards horizontally in a shaking machine 150 times a minute for five hours. It is then ascertained whether the ingredients have separated from one another, if necessary by tests 5 and 6 below. Donarite shows no change.

5. *Behaviour on ignition.* (*a*) Ignition with safety fuze : 3 g. of the powdered explosive are placed in an ordinary test-tube, and a level surface is produced by gentle tapping. On the middle of this surface a piece of slow burning safety fuse (1 metre in 100 secs.) is gently placed and ignited. This experiment is carried out twice with each explosive. Donarite is not ignited.

(*b*) Throwing portions of the powdered explosive into a red-hot iron basin : A hemi-spherical basin 1 mm. thick and 12 cm. diameter is heated to a red heat on the ring of a retort stand by means of a triple burner. At first only small portions are thrown in (0·5 g.). If no detonation takes place, the quantity thrown in at one time is gradually increased up to 5 g. The experiment is repeated twice. Donarite does not explode.

NOTE. The manner in which the explosive burns is observed, and the time that elapses from throwing into the basin to the extinction of the flame.

This test must be carried out with proper precautions. It is recommended that the work be carried out in a good draught and behind two thick sheets of glass. Safety spectacles should also be worn.

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(*c*) Heating small portions to the ignition point in test-tubes placed in a bath of Wood's metal: An iron basin 14 cm. diameter and 7 cm. high is filled to within 2 cm. of the top with Wood's metal. In the centre of the bath a thermometer (0°–360° C.) is immersed 30 mm. deep; it is divided into whole degrees and protected against the effects of explosions. Around the thermometer at a distance of 50 mm. are placed three test-tubes, each 15 mm. internal diameter and 120 mm. long, and immersed 20 mm. deep in the bath. Each test-tube contains 0·2–0·5 g. of the sample, and is placed in the bath at 100°. The temperature of the metal bath is then raised 20° a minute, until ignition occurs or the temperature reaches 320°. Donarite does not ignite below 250°.

NOTE. This test should be carried out behind a protecting screen.

(*d*) Burning large quantities in iron boxes in a wood fire: The box is made of sheet iron, 1 mm. thick; it is cubical in shape, edge 85 mm.; it is riveted and the top edge is turned over 8–9 mm. It has a movable lid and is filled with the explosive (0·5 to 1 kg.). The lid is placed on and fastened with iron wire bound cross-wise round the box, which is then placed in a brisk wood fire and kept there at least ten minutes. The experiment is to be repeated once. Donarite does not explode.

NOTE. This test must be carried out either in the open not less than 100 metres from inhabited buildings, or else in a place that is well protected from the effects of an explosion. The box is to be placed on the fire with care, preferably by means of a mechanism that can be worked from the place of observation. With substances that are not very explosive the box can be laid on by hand, if the place of observation is near; but in this case it should be wrapped up well beforehand in brown paper, so that the explosive may not be ignited too soon through gaps in the iron box.

6. *Mechanical sensitiveness.* (*a*) Blows under the falling weight.

Preparation of the sample. It must be finely divided, and dried twenty-four hours in a vacuum desiccator with calcium chloride, the layer of explosive being not more than 1 cm. thick.

The apparatus consists of a falling weight with an arrangement for suspending it, two rods to guide it, and an anvil of hardened steel let into a support of cast iron in a masonry foundation. About 0·05–0·1 g. of the explosive is spread in a thin layer on the anvil and covered with a short bolt of hardened steel. Instead of laying the explosive loose on the anvil, use may be made of a mould. Every explosive must be tested with a 2 kg. and a 10 kg. weight. At each height of fall six tests are to be carried out, each time with a fresh quantity; in each test the weight is only to be allowed to fall once. The temperature must be 15–20° C. That height at which the explosive begins to detonate regularly (once in six tests) with a distinct report or total ignition is the measure of the sensitiveness. The anvil and bolt are to be cleaned carefully before each test.

(*b*) Friction in an unglazed porcelain mortar.

Preparation of sample, as in 6 (*a*).

The mortar is of unglazed porcelain, 10 cm. internal diameter and 6 cm. high, with an unglazed pestle; the mortar is to be cleaned carefully before the test.

The friction test is to be carried out with 0·05 g. of the substance at the ordinary temperature. The test is to be repeated twice. With Donarite a slight crackling is heard and a little local blackening takes place.

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7. *Addition of water.* Take a cylindrical glass tube about 20 cm. long and 25 mm. wide drawn out at one end ; where it is drawn out place a wad of glass wool and fix the tube vertically. Press 50 g. of the explosive firmly in and pour 100 c.c. of distilled water on to it. The column of water is maintained at its original height by occasional additions, until 50 c.c. have flowed through. No nitro-glycerine must separate from the solution that has come through.

A. II. *Organic Nitro-Compounds and Mixtures containing them.*[1]

As the standard of comparison for nitro-compounds, etc., of Group 1, finely powdered *picric acid* is used with a melting-point not below 120° C. ; for Groups 2 and 3 finely powdered *tetranitro-methyl-aniline* with a melting-point not below 124° C.

The tests consist of :

1. Chemical analysis and establishment of identity (melting-point, etc.).
2. Solubility in water, and tendency to form salts (behaviour towards litmus paper).
3. Exposure to high temperature.
4. Behaviour on ignition.
5. Sensitiveness to mechanical influence (blows, friction).

Preparation of the nitro-compound. Before examination, the substance is to be ground up fine and sifted or otherwise comminuted, and then dried for twenty four hours in a vacuum desiccator over calcium chloride.

1. *Melting-point determination.* A small portion is placed in a fine tube and melted, using an accurate thermometer.

NOTE. This test must be carried out with proper precautions.

2. (*a*) *Solubility in water.* 1 g. of the substance is placed in a stoppered bottle with 100 c.c. of distilled water at 15°–20° C. and shaken repeatedly for half an hour, the undissolved material is then collected on a weighed filter, dried and weighed.

(*b*) *Behaviour to litmus paper.* The solution obtained by (*a*) is tested with sensitive blue litmus paper. In order to detect any red coloration the paper must be washed with water.

(*c*) *Tendency to form dangerous salts.* (i) The solution obtained by (*a*) is left for twenty-four hours in contact with a clean piece of lead sheet free from grease. The solution is removed by washing with water and, if necessary, wiping with a damp pad of cotton-wool, and then it is ascertained whether there has been any action, such as formation of salt.

(ii) 0·5 g. is shaken for five minutes with a solution of 1 g. of sodium hydroxide in 10 c.c. water. To the filtrate an excess of hydrochloric acid is added. A precipitate indicates a tendency to form salts.

(iii) The solution obtained in (2) is slightly acidified with acetic acid and then a little acetate of lead is added. If a precipitate is formed, it is dried and tested for sensitiveness according to paragraph 6 under ammonium nitrate explosives.

3. *Storage of the nitro-compound at 75° C.* As described in paragraph 3 of the

[1] The word nitro-compound is here used in its scientific sense and does not include nitro-cellulose and nitro-glycerine as in the English regulations.

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directions for testing ammonium nitrate explosives. If there be a decided alteration in the appearance or weight of the substance, it should be tested by the methods of paragraph I 6 to see if there has also been an alteration in its sensitiveness. The standard substances show no alteration.

4. *Behaviour on ignition.* (*a*) Ignition with safety fuse. As in 5 (*a*) of the instructions for testing ammonium nitrate explosives. Picric acid is not ignited.

(*b*) Throwing portions into a red-hot iron basin. As in 5 (*b*) of the instructions for testing ammonium nitrate explosives. Picric acid and tetranitro-methyl-aniline do not explode.

(*c*) Heating small portions to the ignition point in test-tubes in a bath of Wood's metal. As in 5 (*c*) of the instructions for testing ammonium nitrate explosives. Picric acid ignites at about 300°, but does not explode. Tetranitro-methyl-aniline ignites at about 190° and puffs off without exploding.

(*d*) Burning a large portion in an iron box in a wood fire. As in 5 (*d*) of the instructions for testing ammonium nitrate explosives. Picric acid burns rapidly but does not explode. Tetranitro-methyl-aniline burns with occasional puffs.

5. *Mechanical sensitiveness.* As in 6 of the instructions for testing ammonium nitrate explosives. When rubbed in the porcelain mortar the standard explosives become brown but do not crackle.

A. III. *Nitrated Chlorhydrins*

There is a danger that nitrated chlorhydrins made from chlorhydrin containing glycerine may contain nitro-glycerine. Any considerable admixture of this kind can be detected by comparing with pure dinitro-chlorhydrin in the falling weight and friction tests (*see* I, 6 (*a*) and (*b*)).

A. IV. *Nitro-cellulose (Gun-cotton, Collodion Cotton)*

The tests consist of :

1. Establishment of identity.
   (*a*) Determination of nitrogen.
   (*b*) Temperature of ignition.
2. Determination of the amount of water or alcohol.
3. Estimation of any additions (potassium or barium nitrate, paraffine).
4. Determination of the stability at 145° C.

1. (*a*) *Nitrogen determination.* This may be carried out by the Schultze-Tiemann (Schlösing) or Lunge method.

1. (*b*) *Temperature of ignition.* About 0·1 g. of the dried nitro-cotton is put into a test-tube 125 mm. long, 15 mm. internal diameter, and 0·5 mm. thick in the wall. This is placed in an oil-bath previously heated to 100° so that exactly 45 mm. of the tube are in the oil and 40 mm. project above the lid of the oil-bath. The middle of the bulb of the thermometer used must be at the same level as the bottom of the test-tube. The temperature of the oil is raised about 5° C. per minute, so that 180° is reached in sixteen minutes.

2. *Percentage of water or alcohol.* 10 gr. of the moist nitro-cellulose are dried

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in a glass basin 30 mm. high and 55 mm. in diameter, provided with a ground-on lid, at 60° C. until the weight is constant. The test is repeated twice.

3. (*a*) *Estimation of additions soluble in water* (potassium, barium nitrate). 10 g. of the dried nitro-cellulose in a weighed filter are washed out with hot distilled water until nothing more goes into solution. The filter with the residue is dried at 60° until the weight is constant.

(*b*) *Paraffine* is determined by extraction with ether.

4. *Stability test at* 145° *C.* Quantities of 0·1 g. dry nitro-cellulose (containing not more than 0·5 per cent. moisture) are placed each in a little glass flask 10 mm. wide and of about 1 c.c. capacity. The flasks are closed by means of tin foil and heated to 145° in the apparatus to be described. Purified nitro-cellulose must withstand the heating for five minutes without igniting.

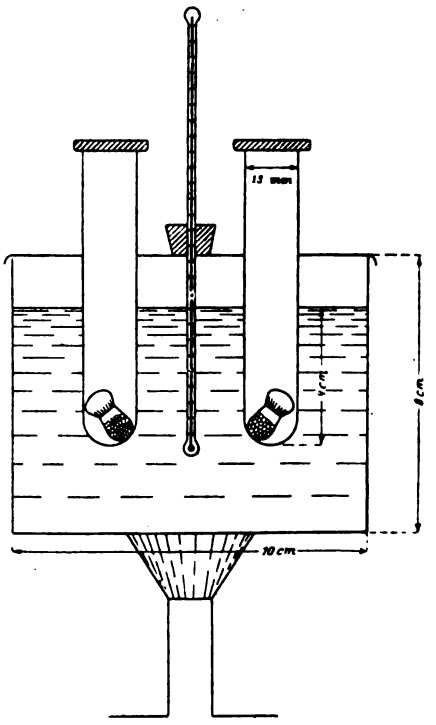

FIG. 137. Stability Test at 145°

The test is carried out as follows: A cylindrical copper bath 10 cm. diameter is filled with machine oil (*see* Fig. 137). The lid has five holes: one is for the thermometer, the other four to take copper tubes, which are inserted with cork stoppers. The tubes must have an internal diameter of 13 mm. and be immersed 4 cm. in the oil. The bottoms of the tubes must be covered with a thin layer of asbestos. When the bath has been heated to 145°, the flasks containing the nitro-cellulose are put into the copper tubes. It is then ascertained whether the four portions ignite in five minutes.

A. V. *Chlorate and Perchlorate Explosives*

As standard of comparison for these explosives in Group 2, *Cheddite* is used, of the composition:

Potassium chlorate	79·0 per cent.
Nitro-naphthalene	1·0 ,,
Dinitro-toluene	15·0 ,,
Castor-oil	5·0 ,,

(The nitro-naphthalene, dinitro-toluene, and castor-oil are melted up together in a water bath, and then the dry finely powdered chemically pure potassium chlorate is uniformly kneaded into the molten mass. Samples are taken and analysed to ascertain that the mixture is uniform.)

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As standard of comparison for Group 3, *Silesia I* is used, of the composition :

Potassium chlorate	85·0 per cent.
Colophony	15·0 „

(Made by intimately mixing the powdered, sifted, dry constituents.)
The tests consist of :

1. Chemical analysis, especially to ascertain the uniformity of the composition.
2. Behaviour to litmus paper.
3. Exposure to high temperature.
4. Exposure to moist and dry air.
5. Shaking test.
6. Behaviour on ignition.
7. Mechanical sensitiveness.

2. *Behaviour to litmus paper.* As in I 2. Cheddite and Silesia I give no acid reaction.

3. *Storage at 75° C.* As in I 3. Cheddite and Silesia I do not alter appreciably.

4. *Exposure alternately to moist and dry air.* Two portions of 100 g. each are kept alternately for forty-eight hours in moist air (under a bell-jar over water) and then forty-eight hours in dry air (in a desiccator). This is done three times. The mechanical sensitiveness is then tested, also the behaviour on ignition, by the methods in I 5 and 6. Cheddite and Silesia I do not alter.

5. *Shaking test.* As in I 4. Cheddite and Silesia I do not alter.

6. *Behaviour on ignition.* (*a*) With safety fuse. As in I 5 (*a*). Cheddite and Silesia I do not ignite.

(*b*) Throwing into red-hot iron basin. As in I 5 (*b*). Cheddite and Silesia I burn rapidly, but do not explode.

(*c*) Determination of ignition point in metal bath. As in I 5 (*c*). Cheddite and Silesia I do not ignite below 200°.

(*d*) Burning in wood fire. As in I 5 (*d*). Cheddite burns rapidly with slight deflagration, Silesia deflagrates vigorously.

7. *Mechanical sensitiveness.* (*a*) Falling weight. As in I 6 (*a*).

(*b*) Friction in mortar. As in I 6 (*b*). Cheddite and Silesia I crackle considerably, but the explosions are only local.

A. VI. *Black Powder and similar Explosives*

As standard of comparison for Group 1 (*d*) *Sprengsalpeter* is used, of the composition :

Sodium nitrate	75 per cent.
Sulphur	10 „
Brown charcoal	15 „

For Group 3 (*d*) a *Sporting Powder* ground to dust and having the composition :

Potassium nitrate	75 per cent.
Sulphur	10 „
Alder charcoal	15 „

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The tests consist of :

1. Chemical analysis.
2. Behaviour to litmus paper.
3. Exposure to high temperature.
4. Behaviour on ignition.
5. Mechanical sensitiveness.

1. *Chemical analysis.* Special care should be taken to ascertain what additional substances are present besides those in the standard explosive.

2. *Behaviour to litmus paper.* As in I 2. The explosives must not be more than slightly acid.

3. *Warm storage.* As in I 3. The standard powder only loses slightly in weight.

4. *Behaviour on ignition.* (*a*) With safety fuse. As in I 5 (*a*). The standard powder burns but does not detonate.

(*b*) In red-hot iron basin. As in I 5 (*b*). Sprengsalpeter ignites after a few seconds and burns away rapidly, but does not detonate ; the sporting powder ignites at once but does not explode.

(*c*) In metal bath. As in I 5 (*c*). The standard powder ignites at about 300°.

5. *Mechanical sensitiveness.* (*a*) Falling weight. As in I 6 (*a*).

(*b*) Friction in mortar. As in I 6 (*b*). The standard powder gives no perceptible reaction.

(A) VII. *Dynamite and similar Explosives*

As standards of comparison *blasting gelatine* and *kieselguhr dynamite* are used, of the composition :

Blasting Gelatine		Kieselguhr Dynamite	
Nitro-glycerine	93 per cent.	Nitro-glycerine	75 per cent.
Collodion cotton	7 „	Kieselguhr	25 „

The tests consist of :

1. Chemical analysis.
2. Behaviour to litmus paper.
3. Exposure to high temperature.
4. Shaking test.
5. Behaviour on ignition.
6. Mechanical sensitiveness.

1. *Chemical analysis.* Quantitative determination of nitro-glycerine, dinitro-glycerine, chlorinated nitro-glycerine, nitro-cellulose, saltpetre, etc.

2. *Behaviour to litmus paper.* As in I 2. Nitro-glycerine explosives containing ammonium nitrate react slightly acid, like donarite.

3. *Warm storage* (at various temperatures). (*a*) Complete cartridges are to be kept for five days at 30°. No nitro-glycerine must sweat out, and after cooling the cartridges must be unchanged.

(*b*) Complete cartridges are to be kept for forty-eight hours at 75°. No red fumes must appear.

4. *Shaking test.* As in I 4.

5. *Behaviour on ignition.* (*a*) With safety fuse. As in I 5 (*a*). Gelatinized

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explosives are cut into small cubes before being put into the test-tube. Guhr dynamite ignites and burns without explosion; blasting gelatine nearly always ignites and burns vigorously without explosion.

(*b*) In red-hot iron basin. As in I 5 (*b*). The standard explosives burn without explosion.

(*c*) In metal bath. As in I 5 (*c*). Guhr dynamite ignites at about 207°–215°, blasting gelatine at about 207°–211°.

(*d*) In wood fire. As in I 5 (*d*). Guhr dynamite ignites and may explode; blasting gelatine detonates.

6. *Mechanical sensitiveness.* (*a*) Falling weight. As in I 6 (*a*).

(*b*) 0·05 g. of the substance is rubbed in an unglazed porcelain mortar with a wooden pestle. The standard explosives do not explode.

B. Propellants

I and II. *Gelatinised Smokeless Powders free from and containing Nitro-glycerine*

The tests consist of:

1. Tests of the materials used in the manufacture of the powder, viz.:

(*a*) The *nitro-cellulose.* It must be of the best quality and pass the following stability tests:

(α) The nitro-cellulose must not give off more than 3 c.c. of nitric oxide per g. in two hours in the Bergmann and Junk test (*see* p. 520).

(β) The temperature of ignition must be above 180° C. as determined by the method given in A IV 1 (*b*).

(*b*) The *nitro-glycerine* must be of the best quality, it must be quite free from acid:

(α) Behaviour to litmus paper. 1 c.c. is shaken with 3 c.c. of distilled water and tested with sensitive blue litmus paper, which must not be coloured red.

(β) With zinc iodide-starch paper at 80°. 1 g. of the nitro-glycerine is to be tested. There must be no violet coloration of the test paper within ten minutes.

2. The *finished powder.* If it is to be classified in Group 1, it must be gelatinized and satisfy the following conditions:

(*a*) Stability test. 1 g. of powder is placed in a thick glass tube 350 mm. long and 19·5 to 20 mm. external diameter, and this is heated to 130° to 132° C. for nitro-cellulose powder, or 120° C. for nitro-glycerine powder. The heating is carried out in the Bergmann and Junk apparatus (*see* p. 520), with the alteration that the tube is closed with a cork instead of with the bulb absorber. The time is observed when light yellowish red fumes appear. With a nitro-cellulose powder they must not be visible before one hour has elapsed at 132°, or with nitro-glycerine powder before one and a half hours at 120°.

(*b*) Ignition point. As in A IV 1 (*b*). The powder is to be tested as far as possible in the form in which it is to be used; it must not be ground. Nitro-cellulose powder must not ignite below 170°, or nitro-glycerine powder below 160° C.

(*c*) Trauzl lead block test. To be carried out according to the method laid down at the Fifth International Congress of Applied Chemistry (*see* p. 385). As a standard of comparison, a nitro-glycerine powder is used made up into cubes with edges 2 mm. long, and consisting of 60 per cent. nitro-cellulose (12 per cent. nitrogen) and

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40 per cent. nitro-glycerine. 10 g. fired with an electric detonator containing a charge of 0·54 g. must not form a cavity more than 10 per cent. larger than that formed by the standard explosive under the same conditions.

(B) III. *Black Powder*

There are no special tests for black powder used as a propellant.

C. Other Explosives

When submitted in the dry state to the following tests they must not show themselves more dangerous than powdered pure picric acid (m.p. not less than 120° C.):

1. *Mechanical sensitiveness.* 0·05 g. is wrapped in tin foil, laid on a block of brass resting on a stone foundation. A sharp-edged iron rod with an under surface of 1 sq. cm. is placed on it, and five hard blows are given with an iron hammer weighing at least 1 kg. This test is carried out five times.

2. *Behaviour on ignition.* As in A I 5 (*a*) and (*b*).

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APPENDIX II

THERMO-CHEMICAL TABLES

Heats of formation, Oxygen compounds of non-metals : Other non-metallic inorganic compounds, Ammonia and its compounds, Compounds of metals : Heats of formation and combustion of organic compounds, Hydrocarbons, Alcohols, solvents, etc., Carbohydrates, Nitro-derivatives, etc. : Latent heats : Specific heats of solids

THE two main authorities on heats of reaction are Berthelot and Thomsen, who have both published fairly comprehensive works on the subject, largely based on their own experiments; but where the actual determinations have been made by others, the results have been brought into general accordance with those of one of the authorities mentioned. The various figures being largely interdependent, it is always best, if possible, to adhere to one set of figures or the other, otherwise considerable errors may be introduced. For instance, Thomsen's figures for the heats of formation of carbon compounds are based on the supposition that they are formed from a porous amorphous form of carbon, which was found by Favre and Silbermann to evolve 96·96 calories when burnt to dioxide ; Berthelot's figures, on the other hand, are calculated from the heat of oxidation of diamond, which is nearly 3 calories less.

In the following Tables only those substances are mentioned which are most likely to occur in calculations connected with explosives.

The Tables are made out on the assumption that all reactions take place under a constant pressure of one atmosphere. Explosive reactions take place in a bomb at constant volume, it is therefore necessary to introduce a correction for the work that would be done by the gases in expanding to atmospheric pressure. At 18°, 0·58 calory, for every mol. of gas generated in the reaction, should be added on to the heat calculated for constant pressure.

The heats of formation are in all cases from the elements and are expressed in large calories per gramme-mol.

In the last column are also given the heats of solution (S) of those products of explosion that are liable to be dissolved by the water formed. Where these have a negative value, it means that the solution produces a fall of temperature. In concentrated solutions, however, the quantities of heat evolved or absorbed are somewhat less. In many cases the quantity of water is insufficient for complete solution.

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HEATS OF FORMATION

Substance	Formula	Heat of Formation		Remarks
		Thomsen	Berthelot	
OXYGEN COMPOUNDS OF NON-METALS				
Water	H_2O	68·36	69·0	liquid
,,	,,	57·93	58·1	gas
Carbon monoxide	CO	29·0	26·1	,,
,, dioxide	CO_2	96·96	94·3	,,
Sulphur dioxide	SO_2	71·1	69·3	gas, rhombic S
,, trioxide	SO_3	103·2	—	liquid
,, ,,	,,	—	103·7	solid
Sulphuric acid	H_2SO_4	210·8	210·1	dissolved
Nitrogen suboxide	N_2O	− 17·7	− 20·6	gas
Nitric oxide	NO	− 21·6	− 21·6	gas
Nitrogen peroxide	N_2O_4	− 2·6	− 1·7	,,
Antimonious acid	H_3SbO_3	167·4	—	solid
Antimonic acid	H_3SbO_4	228·8	—	,,
OTHER NON-METALLIC INORGANIC COMPOUNDS				
Hydrazoic acid (azoimide)	N_3H	—	58·2	dissolved
Ammonium azide	N_4H_4	—	− 19·0	solid
Nitrogen sulphide	NS	—	− 31·9	,,
Antimony sulphide	Sb_2S_3	—	34·4	
Cyanogen	C_2N_2	− 65·7	− 73·8	gas
Hydrocyanic acid	HCN	—	− 24·4	dissolved
Cyanic acid	HCNO	—	37·0	,,
Cyanamide	NH_2CN	—	− 8·2	
Hydrochloric acid	HCl	22·0	22·0	gas
,, ,,	,,	39·3	39·4	dissolved
Hydrogen sulphide	H_2S	2·7	2·3	gas
AMMONIA AND ITS COMPOUNDS				
Ammonia	NH_3	11·9	12·2	gas
,,	,,	20·3	21·0	dissolved
Ammonium chloride	NH_4Cl	75·8	76·8	
,, nitrate	NH_4NO_3	88·05	88·6	
,, carbonate	$(NH_4)_2CO_3$	—	221·6	dissolved
,, bicarbonate	$NH_4.HCO_3$	—	205·3	solid (S, − 6·3)
COMPOUNDS OF METALS				
Sodium chloride	NaCl	97·7	97·9	solid (S, − 1·2)
,, chlorate	$NaClO_3$	86·7	84·8	,,
,, perchlorate	$NaClO_4$	—	100·3	,,

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HEATS OF FORMATION—*continued*

Substance	Formula	Heat of Formation		Remarks
		Thomsen	Berthelot	
COMPOUNDS OF METALS—*continued*				
Sodium nitrate	$NaNO_3$	111·25	110·7	solid
„ carbonate	Na_2CO_3	272·6	270·8	„ (S, + 5·6)
„ bicarbonate	$NaHCO_3$	229·3	227·0	„ (S, − 4·3)
„ sulphide	Na_2S	—	89·3	„ (S, +15·0)
„ tetrasulphide	Na_2S_4	—	99·0	„ (S, + 9·8)
„ sulphate	Na_2SO_4	328·6	328·1	„ (S, + 0·5)
Potassium chloride	KCl	105·6	105·7	solid (S, − 4·4)
„ chlorate	$KClO_3$	95·8	93·8	„
„ perchlorate	$KClO_4$	—	113·5	„
„ sulphide	K_2S	—	103·5	„ (S, +10·0)
„ tetrasulphide	K_2S_4	—	118·6	„ (S, + 1·4)
„ cyanide	KCN	32·5	30·1	„ (S, − 3.0)
„ cyanate	KCNO	—	102·5	„ (S, − 5.2)
„ sulphocyanide	KCNS	—	49·8	„ (S, − 6·1)
„ ferrocyanide	$K_4Fe(CN)_6$	—	137·2	„
„ sulphate	K_2SO_4	344·6	344·3	„ (S, − 6·3)
„ nitrate	KNO_3	119·5	119·0	„
„ carbonate	K_2CO_3	281·1	278·8	„ (S, + 6·5)
„ bicarbonate	$KHCO_3$	—	233·3	„ (S, − 5·3)
Calcium nitrate	$Ca(NO_3)_2$	216·8	202·0	solid
„ carbonate	$Ca(CO_3)_2$	284·5	270·5	„
Barium chlorate	$Ba(ClO_3)_2$	—	171·2	solid
„ perchlorate	$Ba(ClO_4)_2$	—	201·4	„
„ nitrate	$Ba(NO_3)_2$	228·4	227·2	„
„ carbonate	$Ba(CO_3)_2$	285·6	282·5	amorphous
Magnesium oxide	MgO	—	143·3	
„ hydroxide	$Mg(OH)_2$	217·3	217·8	
„ carbonate	$Mg(CO_3)_2$	—	266·6	
Aluminium oxide	Al_2O_3	—	380·2	
„ hydroxide	$Al(OH)_3$	194·5	196·5	
Manganese oxide	MnO	—	90·8	
„ „	Mn_3O_4	—	324·9	
„ dioxide	MnO_2	—	126·0	
Potassium permanganate	$KMnO_4$	194·8	200·0	

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HEATS OF FORMATION—*continued*

Substance	Formula	Heat of Formation		Remarks
		Thomsen	Berthelot	
COMPOUNDS OF METALS—*continued*				
Iron oxide	FeO	—	65·7	
„ „	Fe_3O_4	—	270·8	
Cupric oxide	CuO	—	37·2	
Cuprous oxide . . .	Cu_2O	40·8	43·8	
Lead oxide	PbO	50·3	—	
„ nitrate	$Pb(NO_3)_2$	105·5	—	

The heats of formation of chromium compounds from metallic chromium have not been determined, but Thomsen gives the heat of formation of potassium bichromate from the sesquioxide, potassium and oxygen : K_2, Cr_2O_3, O_4, 15·0 Cals.

HEATS OF FORMATION AND COMBUSTION OF ORGANIC COMPOUNDS

As the heats of combustion have in most cases been determined directly, they are not affected by assumptions as to the quantities of heat liberated in other reactions; but this, of course, does not apply to the heats of formation, which are calculated from the heats of combustion by subtracting the heats of formation of carbon dioxide, water, and any other substances that may be formed.

Thomsen determined the heats of combustion by burning the vapour of the substance with oxygen in a special calorimeter. He could, therefore, only experiment on substances that are volatile : his results are calculated for the substance in the state of gas at 18° burning under constant pressure. Many of the results of Berthelot and others have been obtained in a bomb calorimeter with oxygen under pressure, but the results have been corrected to constant pressure, and refer to the substance in the form in which it exists at the ordinary temperature and pressure. In order to facilitate comparison the heat of volatilization (v) has been given in some instances.

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Substance	Formula	Heat of Formation		Heat of Combustion		Remarks
		Thomsen	Berthelot	Thomsen	Berthelot	
HYDROCARBONS						
Methane	CH_4	21·75	18·9	211·9	213·5	
Ethane	C_2H_6	28·6	23·3	370·4	372·3	
Propane	C_3H_8	35·1	30·5	529·2	528·4	
Ethylene	C_2H_4	− 2·7	−14·6	333·3	341·1	
Acetylene	C_2H_2	−47·8	−58·1	310·0	315·7	
Benzene (vapour)	C_6H_6	−12·5	− 4·1	799·9	785·1	v. 7·3 at 80°
Toluene	C_7H_8	− 3·5	+ 2·3	955·7	933·8	v. 8·0 at 111°
Naphthalene	$C_{10}H_8$	—	−22·8	1233·6	1241·8	solid
ALCOHOLS, SOLVENTS, &c.						
Methyl alcohol	CH_4O	51·45	61·4	182·2	170·6	v. 9·2 at 0°
Ethyl alcohol	C_2H_6O	58·5	69·9	340·5	325·7	v. 10·9 at 0°
Amyl alcohol	$C_5H_{12}O$	74·9	91·6	820·1	793·9	v. 10·7 at 121°
Glycerine	$C_3H_8O_3$	—	160·9	—	397·1	
Ether	$C_4H_{10}O$	70·0	70·5	659·6	651·7	v. 6·6 at 15°
Formaldehyde	CH_2O	—	25·4	—	—	gas (Delépine)
Acetaldehyde	C_2H_4O	48·7	47·5	281·9	279·1	v. 6·0
Acetone	C_3H_6O	58·7	63·0	437·2	426·9	v. 8·1 at 0°
Camphor	$C_{10}H_{16}O$	—	77·7	—	1414·3	
Ethyl acetate	$C_4H_8O_2$	114·7	—	546·6		
Phenol	C_6H_6O	—	36·8	—	736·0	
Cresol (m)	C_7H_8O	—	53·0	—	881·0	
Zinc ethyl	ZnC_4H_{10}	—	2·8	—	—	
Aniline	$C_6H_5NH_2$	−17·4	−11·2	838·5	818·5	v. 9·7 at 183°
Urea	CH_4ON_2	—	80·8	—	151·5	
Guanidine	CH_5N_3	—	19·2	—	247·6	

CARBOHYDRATES

Substance	Formula	Heat of Formation. Berthelot	Heat of Combustion. Berthelot	Remarks
Glucose	$C_6H_{12}O_6$	302·6	677·2	
Cane sugar	$C_{12}H_{22}O_{11}$	535·6	1355·0	
Dextrine	$C_6H_{10}O_5$	243·6	667·2	
Starch	,,	225·9	684·9	
Cellulose	,,	230·4	681·8	
Wood meal	$C_{50}H_{72}O_{33}$	1500	5700	

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The figures for wood meal have been calculated from the mean of the results that have been published, using Berthelot's heat of formation of carbon dioxide. The figures for the other carbohydrates are due to Berthelot and his collaborators.

NITRO-DERIVATIVES, ETC.

Substance	Formula	Heat of Formation. Berthelot	Heat of Combustion. Berthelot	Remarks
Nitrobenzene . .	$C_6H_5NO_2$	5·1	—	liquid
o-dinitrobenzene . .	$C_6H_4(NO_2)_2$	0·3	703·5	solid
m- ,, . .	,,	6·8	697·0	,,
p- ,, . .	,,	8·4	695·4	,,
1.3.5 trinitrobenzene .	$C_6H_3(NO_2)_3$	5·5	663·8	
1.2.4 ,, .	,,	−9·2	678·5	
Picric acid . . .	$C_6H_3N_3O_7$	49·1	618·4	
Potassium picrate .	$C_6H_2N_3O_7K$	117·5	619·7	bicarb. K
Ammonium picrate .	$C_6H_6N_4O_7$	80·1	690·9	
Diazobenzene nitrate .	$C_6H_5N_3O_3$	−47·4	782·9	
Mercury fulminate .	$C_2N_2O_2Hg$	−62·9	250·9	Hg free
Glycerine mononitrate .	$C_3H_7NO_5$		385·2	Will
,, dinitrate α (dry)	$C_3H_6N_2O_7$	—	380·0	,,
,, dinitrate α (crys)	$C_3H_6N_2O_7$, $\frac{1}{3}H_2O$	—	373·3	,,
,, dinitrate β .	$C_3H_6N_2O_7$	—	374·0	,,
,, trinitrate .	$C_3H_5N_3O_9$	—	363·2	,,
,, ,, .	,,	94·2	361·2	Berthelot
Guncotton . . .	$C_{24}H_{29}N_{11}O_{42}$	624	—	Berthelot
		546	—	for 1 kg.
,, . . .	13 per cent. N	544	—	for 1 kg.[1]
Collodion cotton . .	$C_{24}H_{31}N_9O_{38}$	696	2629·5	Berthelot
Trinitrotoluene . .	$C_7H_5N_3O_6$	7·7	—	from Bichel's figures
Nitrophenol (o) . .	$C_6H_5NO_3$	50·1	688·2	solid, Matignon
,, (p) . .	,,	49·2	689·1	,, ,,
Guanidine nitrate . .	$CH_6N_4O_3$	93·5	207·8	Matignon
Nitro-guanidine . .	$CH_4N_4O_2$	22·0	210·3	,,
Diphenylamine . .	$C_{12}H_{11}N$	−29·4	1536·9	Stohmann

For nitro-aromatic compounds Berthelot gave the rule that the introduction of a nitro-group increases the heat of formation by 9 calories. The knowledge we now possess shows that this value is too high in many cases. The heats of formation of the nitro-derivatives of the aromatic hydrocarbons are, like those of the parent substances, very small, and may be either positive or negative, the value depending more upon the distribution of the nitro-groups than upon their number. For a compound of this class, the heat of formation of which has not been determined, no great error will be introduced if it be assumed that it is 0 (C, diamond).

[1] This is a mean result calculated by the author from the figures of Noble (*Proc. R. S.*, 1894) and others, using Berthelot's heats of formation, and correcting to constant pressure.

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LATENT HEATS (Cals. per g. Atom)

Substance	M.p.	Heat of Fusion	Temperature of Vapour	Heat of Vaporisation
Lead	326°	1·1		
Iron	1000°	1·9		
Sulphur	115°	0·3	316°	11·6
Tin	228°	1·6		
Mercury	− 39°	0·6	358°	13·6
Aluminium	625°	6·5[1]		

SPECIFIC HEATS OF SOLIDS

(Heat in small calories required to raise temperature 1° C.)

Substance	Symbol	Temperature	Specific Heat	Molecular Heat	Authority
Aluminium	Al	15°–185°	·219	5·94	Tilden
		10°	·222	6·01	Richards
		600°	·282	7·65	,,
Lead	Pb	15°	·0299	6·20	Naccari
		200°	·0324	6·71	,,
		300°	·0338	7·00	,,
Iron (steel)	Fe	0°–18°	·1066	5·95	Hill
		20°–100°	·1178	6·63	,,
		500°	·1764	9·85	Pionchon
		700°	·3243	18·1	,,
		720°–1000°	·218	12·2	,,
		1000°–1200°	·199	11·1	,,
Carbon (charcoal)	C	0°–24°	·1653	1·99	Weber
		0°–224°	·2385	2·86	,,
(graphite)		10·8°	·1604	1·92	,,
		138°	·2542	3·06	,,
		977°	·4670	5·60	,,
		0°–2000°	·475	5·70	Violle
		0°–3000°	·535	6·32	,,
Copper	Cu	20°–100°	·0936	5·95	Schmitz
		900°	·1259	8·00	Richards
		780°–1000°	·118	7·51	Le Verrier

[1] This is the total heat required to heat 27·1 g. of aluminium from 0° to 625° and melt it.

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SPECIFIC HEATS OF SOLIDS—*continued*

Substance	Symbol	Temperature	Specific Heat	Molecular Heat	Authority
Mercury	Hg	0°	·0334	6·76	Naccari
		250°	·0321	6·44	,,
Sulphur	S	17°–45°	·163	5·22	Kopp
(liquid)		116°–136°	·2317	7·43	Classen
(viscous)		160°–201°	·279	8·95	Dussy
		201°–233°	·331	10·6	,,
		233°–264°	·324	10·4	,,
Tin	Sn	19°–99°	·0552	6·57	Voigt
		16°–197°	·0588	7·00	Spring
(liquid)		250°–350°	·0637	7·58	Person
		1100°	·0758	9·02	Pionchon
Aluminium oxide	Al_2O_3	26°	·2003	20·5	Russell
Antimony oxide	Sb_2O_3	18°–100°	·0927	26·5	Neumann
Lead oxide	PbO	22°–98°	·0512	11·4	Regnault
Iron oxide	Fe_3O_4	24°–99°	·1678	38·8	,,
Copper oxide	CuO	12°–98°	·1420	11·3	,,
Magnesium oxide	MgO	24°–100°	·2439	9·63	,,
Quartz	SiO_2	20°–50°	·186	11·2	Kopp
		0°	·1737	10·4	Pionchon
		350°	·2786	16·8	,,
		400°–1200°	·305	19·4	,,
Tin oxide	SnO_2	16°–98°	·0933	14·1	Regnault
Potassium chloride	KCl	14°–99°	·1730	12·9	,,
Sodium chloride	NaCl	15°–98°	·2140	12·5	,,
Potassium sulphate	K_2SO_4	15°–98°	·1901	33·1	,,
Sodium sulphate	Na_2SO_4	17°–98°	·2312	32·8	,,
Potassium hyposulphite	$K_2S_2O_3$	20°–100°	·197	37·5	Pape
Sodium hyposulphite	$Na_2S_2O_3$	25°–100°	·221	36·5	,,

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SPECIFIC HEATS OF SOLIDS—*continued*

Substance	Symbol	Temperature	Specific Heat	Molecular Heat	Authority
Barium carbonate .	$BaCO_3$	11°–99°	·1104	21·7	Regnault
Calcium carbonate (aragonite)	$CaCO_3$	16°–45°	·203	20·3	Kopp
		0°–100°	·2065	20·6	Lindner
		0°–200°	·2121	21·2	,,
		0°–300°	·2176	21·8	,,
Potassium carbonate .	K_2CO_3	23°–99°	·2162	29·9	Regnault
Sodium carbonate .	Na_2CO_3	16°–98°	·2728	29·0	,,
Silicates . . .	—	0°–100°	·17–·21	—	Various

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APPENDIX III

CONVERSION OF UNITS

Pressure

	Atmosphere	Kg./sq. cm.	Tons./sq. in.
1 atmosphere	1	1·033	·006562
1 kg. per sq. cm.	·9678	1	·006350
1 ton per sq. in.	152·4	157·5	1

Mechanical Equivalent of Heat

424 kilogramme-metres = 1 Calory (large)

Temperature

c = °C. f = 1·8 c + 32.
f = °F. c = ·555 (f − 32).

Length

1 inch	=	25·40 mm.	1 millimetre	=	·03937 in.
1 foot	=	30·48 cm.	1 centimetre	=	·03281 ft.
1 yard	=	·9144 m.	1 metre	=	1·094 yd.

Capacity

1 pint	=	·5679 litre.	1 litre	=	1·761 pint.
1 gallon		4·543 litre.	1 litre	=	·2201 gallon.

Weight

1 grain	=	·06480 g.	1 gramme	=	15·43 gr.
1 ounce (av.)		28·35 g.	1 gramme		·03527 oz.
1 pound (av.)		453·6 g.	1 kilogramme		2·205 lb.
1 ton		1016·0 kg.	1 metric ton		·984 ton.

1 gallon contains 10 lb. of water at 62° F.
1 litre contains 1 kg. of water at 4° C.

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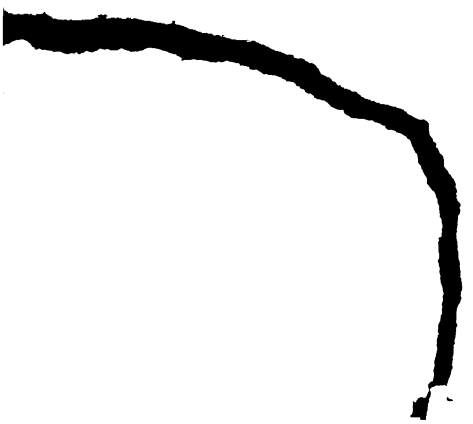

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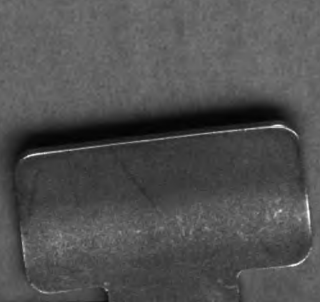

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